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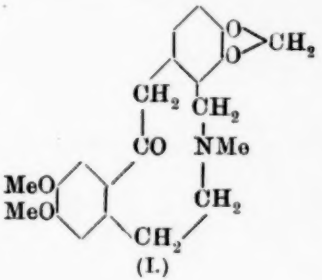
LX.—*Cryptopine. Part II.*

By WILLIAM HENRY PERKIN, jun.

THE present investigation was originally undertaken with the object of clearing up some points, difficult of explanation, which had arisen during the course of the experiments described in Part I of this research.* Gradually the scope of the inquiry has widened, and many developments are included in this communication which were at first not contemplated. Broadly speaking, the basis of the new material is the series of changes represented by the conversion of cryptopine (I) into *iso*cryptopine chloride (II), and the formation of anhydrocryptopine (III) from the latter by the elimination of hydrogen chloride (833, 850).†



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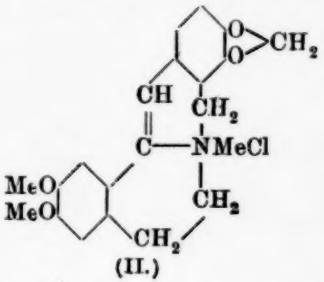

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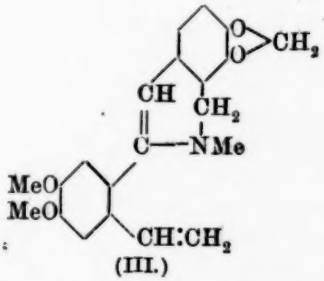

(III.)

It was shown in the earlier research (852) that the properties of anhydrocryptopine are in many respects quite unusual, and one of the points most difficult of explanation is the behaviour of anhydrocryptopine methosulphate (or the corresponding methochloride) towards hydrolytic agents. Normally, the hydrolytic

* "Cryptopine and Protopine," Part I., T., 1916, **109**, 815—1028.

† The numbers in brackets—thus (833)—refer to the page in Part I.

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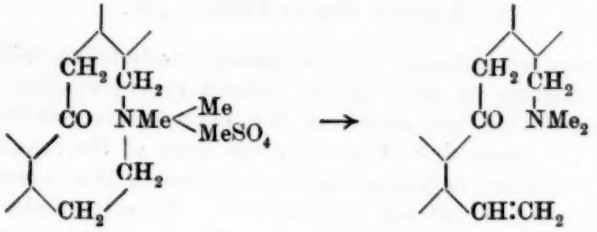
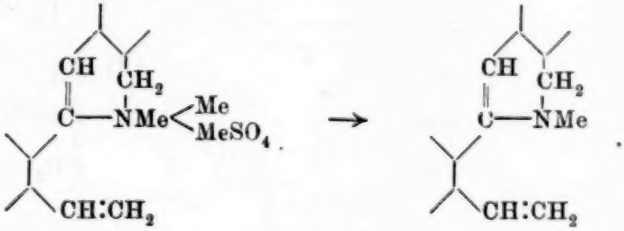
decomposition of a methosulphate results in the formation of a new base containing a methyl group more than the original base contained. Thus cryptopine methosulphate is decomposed on hydrolysis with the formation of methylcryptopine (847).



The methosulphate of anhydrocryptopine does not behave in this way (852), but is hydrolysed by methyl-alcoholic potassium hydroxide with elimination of the added methyl group and regeneration of anhydrocryptopine.

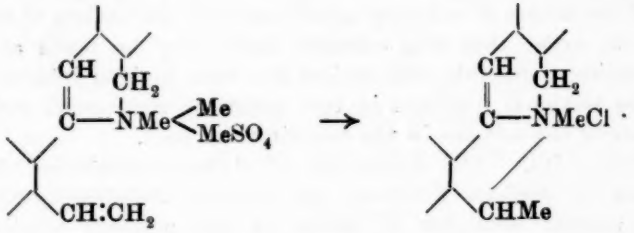


A case of this kind does not appear to have been previously recorded, and although an attempt was made (854; T., 1918, **113**, 735) to find some explanation for this curious removal of a methyl group from nitrogen, it is still not clear why the *N*-methyldihydro-*iso*quinoline ring characteristic of anhydrocryptopine should exhibit this unusual behaviour. Recently (T., 1918, **113**, 735), a welcome confirmation of the curious change just mentioned has been forthcoming, since it has been found possible to prepare from berberine the derivative—anhydromethylberberine—which corresponds exactly with anhydrocryptopine.

This substance also combines readily with methyl sulphate to yield the corresponding methosulphate, which, when boiled with methyl-alcoholic potassium hydroxide, is decomposed in exactly the same manner as anhydrocryptopine methosulphate, with regeneration of anhydromethylberberine.

Not only do alkali hydroxides cause the elimination of a *N*-methyl group from anhydrocryptopine methosulphate, but experiment has shown that a process of the same kind occurs even

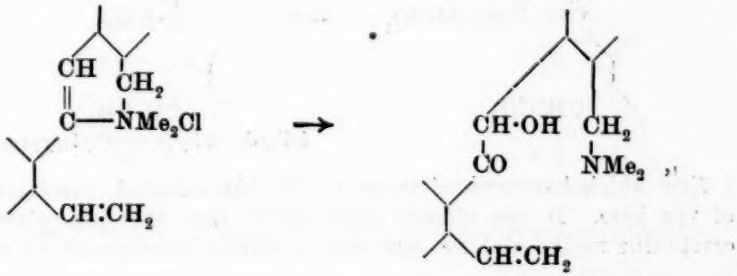
more readily when acid reagents are employed. Thus anhydrocryptopine methosulphate is rapidly changed by boiling with concentrated hydrochloric acid, and ψ-cryptopine chloride is produced, a decomposition which appears to be correctly represented by the scheme (855):



An exactly analogous change is observed when anhydromethylberberine methosulphate is digested with concentrated hydrochloric acid, ψ-methylberberinium chloride being obtained (T., 1919, **113**, 735).

In the present communication (p. 767), it is shown that concentrated mineral acid need not be employed in order to bring about the elimination of the *N*-methyl group, since ψ-cryptopine chloride is readily obtained when anhydrocryptopine methosulphate is heated on the steam-bath with dilute hydrochloric acid, and ψ-cryptopine hydrogen sulphate, $C_{21}H_{22}O_4N{\cdot}HSO_4$, results, in a similar manner, from the action of dilute sulphuric acid on the methosulphate.

The remarkable changes associated with the action of hydrolytic agents on anhydrocryptopine methosulphate suggested the desirability of making a further study of the behaviour of this substance towards other reagents. Experiments on the oxidation of the methosulphate did not lead to useful results, but the corresponding methochloride is oxidised by permanganate, without elimination of an *N*-methyl group and with the formation of a base, $C_{22}H_{25}O_6N$ (m. p. 188°), which appears to be produced according to the scheme:



and has been named *dioxymethylisoanhydrodihydrocryptopine* (p. 738).

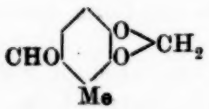
Of much greater interest is the behaviour of anhydrocryptopine methosulphate when subjected to the action of reducing agents, and it was the results obtained during the study of these remarkable changes which led to the extension of the subject so as to include the action of reducing agents on other derivatives of cryptopine. In order that this complex study may be made as clear and concise as possible, the subject has been divided into sections, and the sectional numbers in this summary correspond with the numbers of the sections in the experimental part.

Section I (a). *The Reduction of Anhydrocryptopine Methosulphate by Sodium Amalgam in Alkaline Solution* (p. 740).—When sodium amalgam is added to the aqueous solution of anhydrocryptopine methosulphate, a base, $C_{22}H_{25}O_4N$—*dihydroanhydromethylcryptopine*—gradually separates, which has not been obtained crystalline, but yields a crystalline methosulphate,

$$C_{22}H_{25}O_4N,Me_2SO_4,$$

and methiodide, $C_{22}H_{25}O_4N,MeI$. It is clear, therefore, that elimination of a methyl group had not taken place during reduction under these conditions.

On oxidation in acetone solution with permanganate, the new base yields 5:6-methylenedioxy-*o*-tolualdehyde (907) and 5:6-methylenedioxy-*o*-toluic acid (916),



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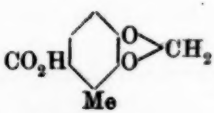

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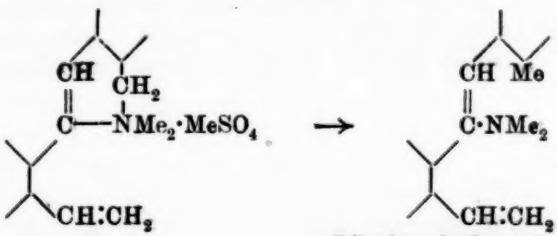
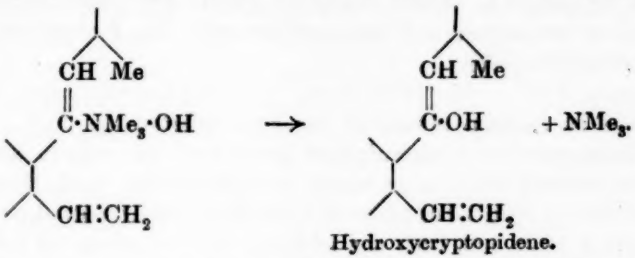
It is clear, therefore, that its formation from anhydrocryptopine methosulphate is probably represented thus:



Dihydroanhydromethylcryptopine.

a view which has received support from the detailed investigation of the base. It has already been stated that the base yields a crystalline methosulphate, and this is readily decomposed by boil-

ing with methyl-alcoholic potassium hydroxide, with elimination of trimethylamine and formation of a new substance, $C_{20}H_{20}O_5$:



Hydroxycryptopidene.

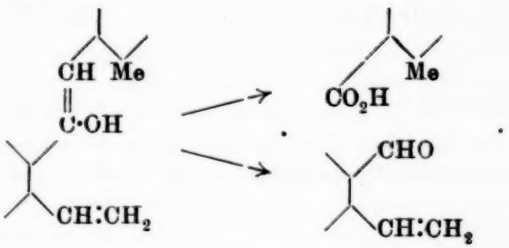
Hydroxycryptopidene * melts at 88—90°, and yields, on oxidation with permanganate, 5 : 6-methylenedioxy-*o*-toluic acid,

$$CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H$$

(916), and 4 : 5-dimethoxy-2-vinylbenzaldehyde,

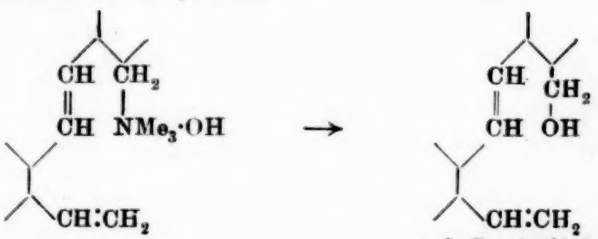
$$(MeO)_2C_6H_2(CHO){\cdot}CH{:}CH_2$$

(904), the former containing the upper and the latter the lower portion of the molecule.



This fission clearly demonstrates the constitution of the substance, $C_{20}H_{20}O_5$, and indirectly that also of dihydroanhydromethylcryptopine.

Hydroxycryptopidene is isomeric and closely allied with α-*iso*cryptopidol (m. p. 92°; 843), which results in a similar manner from methyl*iso*anhydrodihydrocryptopine methosulphate by the elimination of trimethylamine:

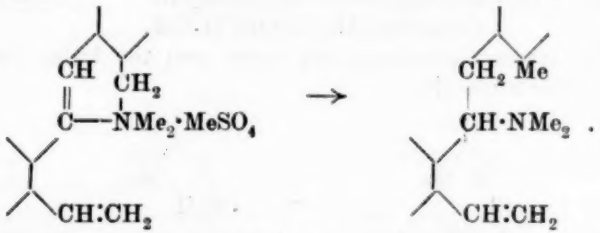


α-*iso*Cryptopidol.

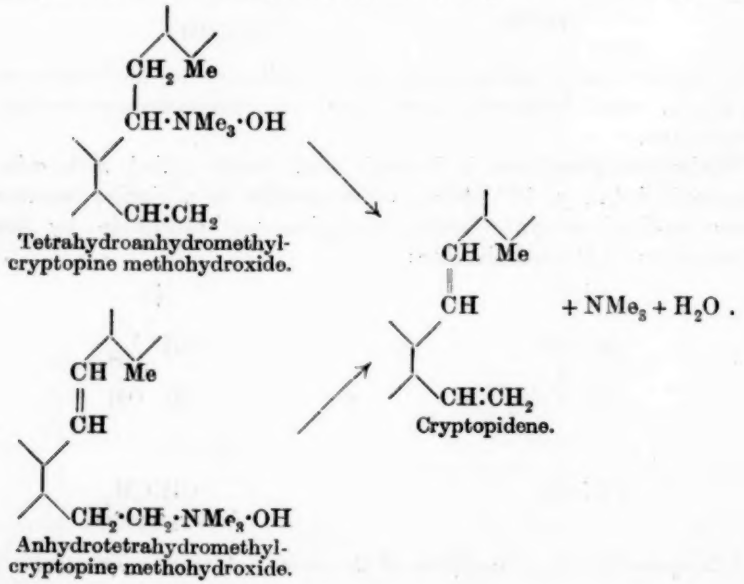
* Compare (926) for a description of the parent substance cryptopidene.

Hydroxycryptopidene does not yield an acetyl derivative, but is converted by the action of acetyl chloride into a polymeric modification, $(C_{20}H_{20}O_5)_n$, which melts at about 200°, and corresponds closely in properties and composition with the β-modification of *iso*cryptopidol (843).

Section I (b). *The Reduction of Anhydrocryptopine Methosulphate by Sodium Amalgam in Acid Solution* (p. 743).—When anhydrocryptopine methosulphate is reduced by sodium amalgam in the presence of a large excess of hydrochloric acid, disruption of the central ring takes place in a manner similar to that described in Section I (*a*), but with the addition of four atoms of hydrogen and again without the elimination of a methyl group. The product is a base, $C_{22}H_{27}O_4N$—*tetrahydroanhydromethylcryptopine*—and its properties are in harmony with its formation, according to the scheme:

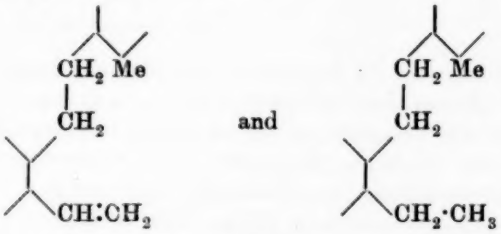


This base has not been obtained crystalline, and is isomeric with anhydrotetrahydromethylcryptopine (898), which is crystalline



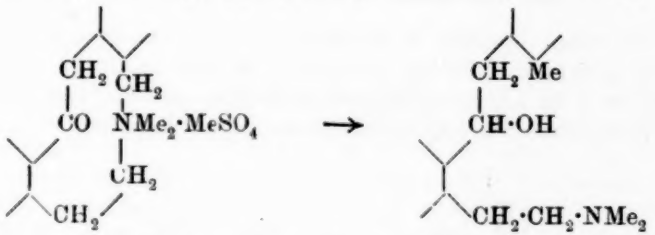
and melts at 107°. The close relationship between these bases is well brought out when their formulæ are written side by side and by the fact that the methosulphates of both are decomposed by boiling with methyl-alcoholic potassium hydroxide, with elimination of trimethylamine and separation of cryptopidene (m. p. 123°; see above).

A further stage in the reduction of the cryptopine molecule has been achieved by the preparation of *dihydrocryptopidene*, $C_{20}H_{22}O_4$ (m. p. 128°), and the reduction of cryptopidene to *tetrahydrocryptopidene*, $C_{20}H_{24}O_4$:



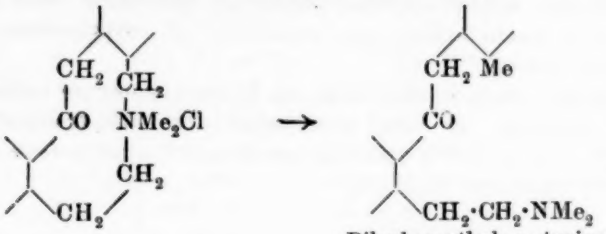
The first of these is obtained by a process described on p. 762, and the latter is produced when cryptopidene is reduced in boiling alcoholic solution with sodium. It is one of the most beautiful substances in the cryptopine series, melts at 78°, and crystallises in stout, colourless prisms (p. 745).

Section II (p. 746). *The Reduction of Cryptopine Methochloride in Alkaline Solution.*—The conversion of cryptopine methosulphate into tetrahydromethylcryptopine by reduction in strongly acid



solution with sodium amalgam is described in Part I of this research (821 and 826), and the present object was to determine whether, during this process, the reduction of the keto-group precedes the fission of the ring or vice versâ. Since further experiments on the reduction of the methosulphate did not yield information of value, the effect of reducing agents on the corresponding methochloride was investigated. The interesting fact was then observed that, whilst cryptopine methochloride, when reduced in alkaline solution with sodium amalgam, is converted in the

main into tetrahydromethylcryptopine, there is also formed in small quantity a new base, $C_{22}H_{27}O_5N$, which melts at 118—120°, and is obviously produced according to the scheme:



Dihydromethylcryptopine.

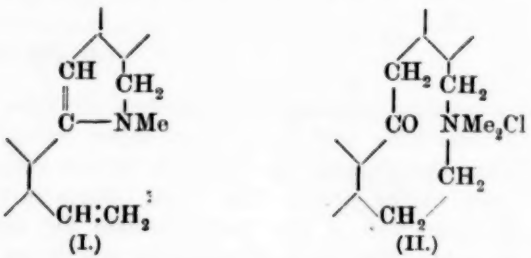
that is to say, during its formation, the ten-membered ring has been ruptured before the reduction of the keto-group.

The constitution assigned to dihydromethylcryptopine receives support from the fact that, when oxidised with permanganate, the base yields 5:6-methylenedioxy-*o*-tolualdehyde and 5:6-methylenedioxy-*o*-toluic acid (compare p. 747). The isolation of this base would seem to indicate that the first action of the alkaline reducing agent on cryptopine methochloride is fission of the ten-membered ring, but that most of the dihydromethylcryptopine, thus produced, suffers further reduction before it can be removed from the sphere of action of the excess of the reducing agent.

Section III.

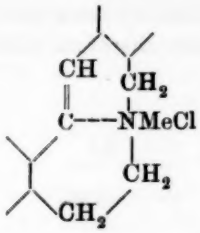
The Reduction of iso*Cryptopine Chloride.*

In the cases discussed in Sections I and II, the groups of atoms taking part and suffering disruption as the result of reduction belong in I to a single dihydro*iso*quinoline nucleus, and in II to the ten-membered group characteristic of cryptopine:



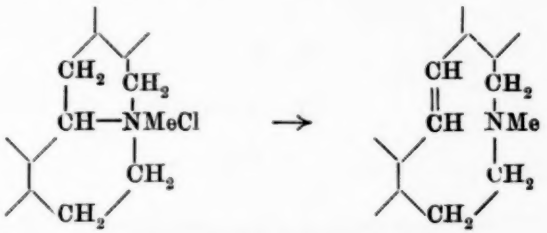
(I.) (II.)

It was next desired to investigate what the effect of reduction might be in the case of a substance containing a partly reduced double *iso*quinoline ring, and *iso*cryptopine chloride (833) was

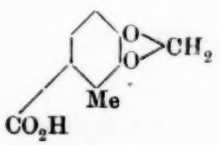


selected for this purpose. The effect of reduction was again studied (*a*) in alkaline and (*b*) in acid solution.

Section III (a). *The Reduction of* iso*Cryptopine Chloride in Alkaline Solution* (p. 748).—Since *iso*cryptopine chloride is very sparingly soluble in cold water, the reduction with sodium amalgam could only be carried out effectively on the steam-bath, and, under these conditions, a resinous base separates, and the liquid, on cooling, becomes filled with a voluminous mass of needles of a quaternary salt. This salt, which is produced in considerable quantity, was readily identified as *iso*dihydrocryptopine β-chloride, since, on boiling with methyl-alcoholic potassium hydroxide, it yielded anhydrodihydrocryptopine (*A*) (938):



One of the main directions in which *iso*cryptopine chloride suffers reduction is therefore simply by the addition of hydrogen to the double linking without disruption of either ring. The resinous base may be separated, by fractional crystallisation, into two new substances, namely, a very sparingly soluble base, $C_{21}H_{23}O_4N$, melting at 195°, which is present in very small quantity, and considerable quantities of a readily soluble base, $C_{21}H_{25}O_4N$, which melts at 138°. The base, $C_{21}H_{23}O_4N$, yields, on oxidation, 5:6-methylenedioxy-*o*-toluic acid (916), and apparently



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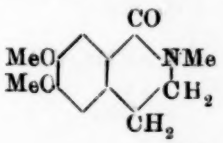
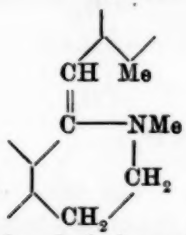


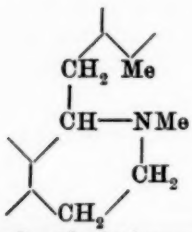
also 1-keto-6:7-dimethoxy-2-methyltetrahydro*iso*quinoline (Pyman, T., 1909, **95**, 1268), and must therefore have the constitution



Dihydroanhydro*iso*cryptopine.

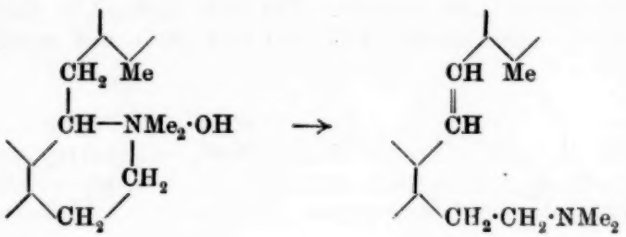
This base is therefore produced from *iso*cryptopine chloride by the rupture of the upper dihydro*iso*quinoline ring without reduction of the double linking.

The readily soluble base, $C_{21}H_{25}O_4N$, melting at 138°, yields 5:6-methylenedioxy-*o*-tolualdehyde (and acid), as well as 1-keto-6:7-dimethoxy-2-methyltetrahydro*iso*quinoline, on oxidation with permanganate, and must therefore be the dihydro-derivative of the base just described (m. p. 195°) and have the constitution



Tetrahydroanhydro*iso*cryptopine.

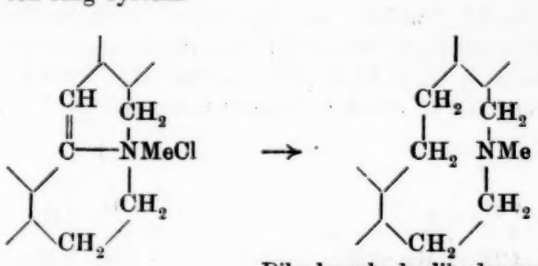
It yields very characteristic salts and other derivatives, of which the *methosulphate*, $C_{21}H_{25}O_4N,Me_2SO_4$ (m. p. 160°), and *methiodide*, $C_{21}H_{25}O_4N,MeI$ (m. p. 263°), crystallise particularly well. When boiled with methyl-alcoholic potassium hydroxide, the methosulphate is readily decomposed, with the formation of anhydrotetrahydromethylcryptopine, a base which had previously



been obtained, in the form of its hydrochloride, from tetrahydromethylcryptopine by the action of phosphoryl chloride (899).

Section III (b). *The Reduction of* iso*Cryptopine Chloride in Acid Solution* (p. 749).—Reduction takes place readily when the hot solution of *iso*cryptopine chloride in a mixture of dilute acetic and hydrochloric acids is treated with a large excess of sodium amalgam, and leads to the formation of two bases, $C_{21}H_{25}O_4N$, melting at 138° and 164° respectively, as well as of considerable quantities of *iso*dihydrocryptopine β-chloride.

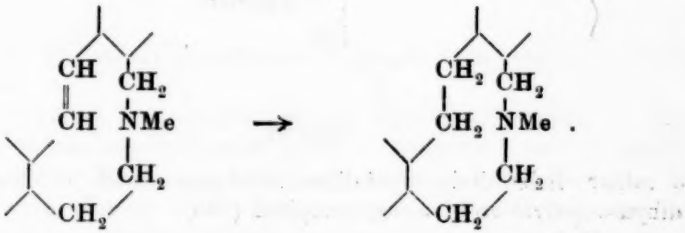
The base melting at 138° is tetrahydroanhydro*iso*cryptopine, identical with that isolated from the product of the alkaline reduction of *iso*cryptopine chloride. The second base, melting at 164°, which does not appear to be one of the products of the alkaline reduction, is *dihydroanhydrodihydrocryptopine* (*A*), and, in its formation, not only has the ethenoid linking in *iso*cryptopine been reduced, but the double *iso*quinoline ring has also suffered disruption in a very remarkable manner, with the formation of a fully saturated ten-ring system.



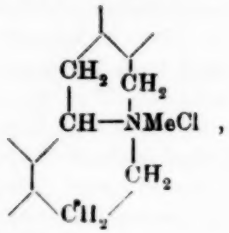
Dihydroanhydrodihydrocryptopine (*A*).

This base is remarkably stable to permanganate, and does not yield 5:6-methylenedioxy-*o*-toluic acid on oxidation, showing that reduction has not resulted in the formation of the group $CH_2{:}O_2{:}C_6H_2Me{\cdot}CH{:}$ (p. 716).

The definite proof of its constitution was obtained as the result of the observation that the base in question is readily produced when anhydrodihydrocryptopine (*A*) (938) is reduced by sodium amalgam in acid solution.

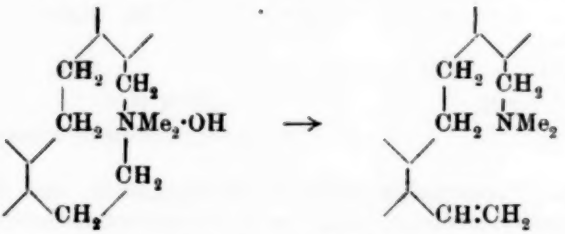


The curious formation of dihydroanhydrodihydrocryptopine (*A*) from *iso*cryptopine chloride by reduction is dependent in some way on the presence of the ethenoid linking in one of the reduced *iso*quinoline rings, a condition which apparently causes strain, and consequent instability. That this is so is indicated by the fact that, when this ethenoid linking is not present, scission does not appear to take place. Thus, for example, all attempts to reduce tetrahydroberberine methochloride, which contains the grouping

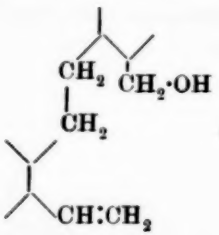


have been unsuccessful.

Dihydroanhydrodihydrocryptopine (*A*) yields a methosulphate, $C_{21}H_{25}O_4N,Me_2SO_4$, which, on hydrolysis with methyl-alcoholic potassium hydroxide, is converted into *dihydroisoanhydrodihydromethylcryptopine*, $C_{22}H_{27}O_4N$ (945), a beautiful substance melting at 77°, the crystals of which have been measured (p. 757).

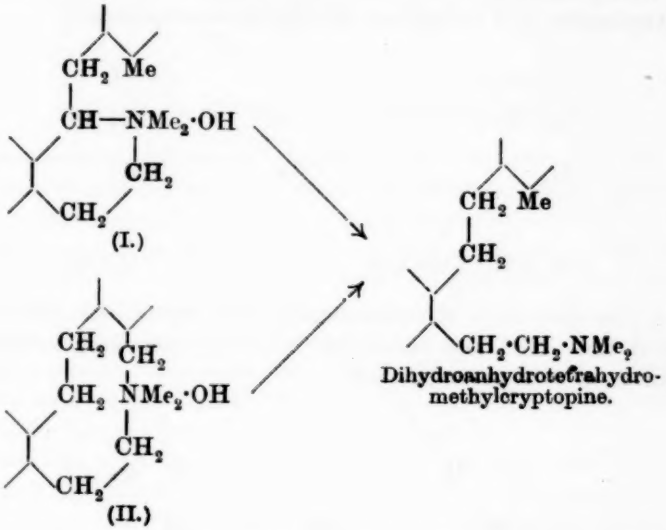


Finally, the methosulphate of this base, $C_{22}H_{27}O_4N,Me_2SO_4$, is decomposed by boiling with methyl-alcoholic potassium hydroxide, with the separation of *dihydro*-α-iso*cryptopidol*,



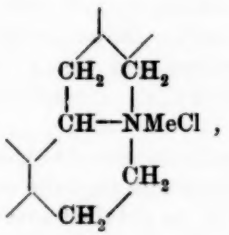
a rather indefinitely crystalline substance which is clearly the dihydro-derivative of *α-iso*cryptopidol (948).

Section III (c). *Dihydroanhydrotetrahydromethylcryptopine* (p. 759).—This substance is produced from the methosulphate either of tetrahydroanhydro*iso*cryptopine (I, m. p. 138°, p. 722) or of dihydroanhydrodihydrocryptopine (*A*) (II, m. p. 164°, p. 723) by reduction in alkaline solution with sodium amalgam:



Dihydroanhydrotetrahydromethylcryptopine.

The other cases of ring-fission during reduction, described in this communication, occur in systems in which the ring in question is unsaturated, and it is pointed out on p. 724 that attempts to reduce the completely saturated system,

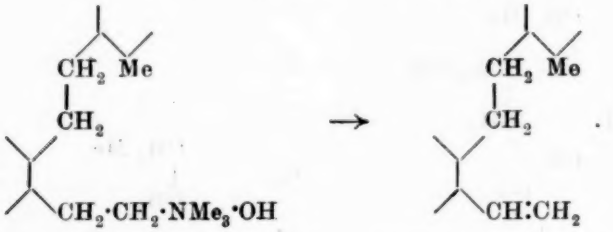


contained in tetrahydroberberine methochloride, have not been successful.

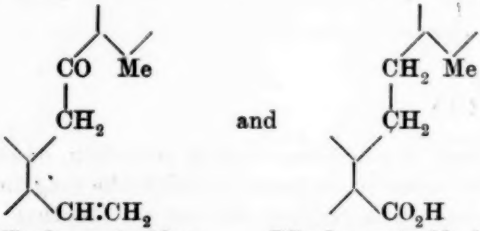
It is therefore remarkable that the removal of a bridge in this complex in the two directions shown in formulæ I and II should so weaken the structure as to make it susceptible to reduction. It is, of course, possible that the accumulation of methyl groups on the nitrogen atom may tend to weaken the structure, and a good

deal of evidence is to be found in this communication in favour of that view.

Dihydroanhydrotetrahydromethylcryptopine melts at 63°, and is characterised by yielding a very sparingly soluble hydrochloride. The *methosulphate*, $C_{22}H_{29}O_4N,Me_2SO_4$, is decomposed by boiling with methyl-alcoholic potassium hydroxide, with elimination of trimethylamine and formation of *dihydrocryptopidene*.



This new derivative of cryptopidene (926) crystallises splendidly, melts at 126—128°, and yields the following interesting substances on oxidation with permanganate:



Ketodihydrocryptopidene. Dihydrocryptopidenic acid.

Ketodihydrocryptopidene melts at 116° and yields a *semicarbazone*, $C_{21}H_{23}O_5N_3$, melting at 190°. *Dihydrocryptopidenic acid* is a very sparingly soluble, crystalline acid (m. p. 194—195°), the *anilide* of which, $C_{18}H_{19}O_4·CO·NH·C_6H_5$, crystallises in needles and melts at 185°.

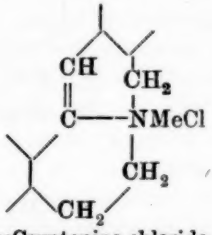
The degradation of cryptopine to this acid is particularly interesting, and it is unfortunate that the small amount of material available did not allow of its detailed investigation.

Section IV.

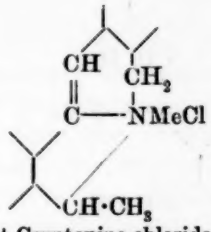
The Reduction of ψ-Cryptopine Chloride.

The conversion of anhydrocryptopine methosulphate into ψ-cryptopine chloride is mentioned on p. 715 (compare 855 and 984), and the similarity in constitution between this substance and

*iso*cryptopine chloride is obvious when their formulæ are compared:



*iso*Cryptopine chloride.



ψ-Cryptopine chloride.

The essential difference between these formulæ is the fact that, whereas in *iso*cryptopine chloride the central portion consists of two reduced *iso*quinoline rings fused together, the molecule of ψ-cryptopine chloride contains only one such ring. When the bridge across the molecule is removed by reduction, the result in the case of *iso*cryptopine chloride is the formation of a ten-membered ring (p. 723), whereas if a similar change is assumed to take place in the molecule of ψ-cryptopine chloride, reduction should lead to the formation of a nine-membered ring system, of which, so far, few examples have been described.

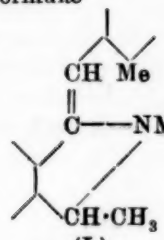
Since the investigation of this matter seemed to offer attractive possibilities, the problem has been carefully studied, and it may be said at once that the comparatively slight difference in constitution which ψ-cryptopine chloride exhibits in comparison with *iso*cryptopine chloride is sufficient to give rise to wide differences in behaviour when the two substances are reduced under similar conditions.

Section IV (a). *The Reduction of ψ-Cryptopine Chloride in Alkaline Solution* (p. 769).—ψ-Cryptopine chloride, $C_{21}H_{22}O_4NCl$, is readily reduced in slightly alkaline aqueous solution by sodium amalgam at the temperature of the steam-bath, and a base, $C_{21}H_{23}O_4N$, separates, which crystallises from methyl alcohol in stout prisms and melts at 112°.*

This base is produced by the addition of two atoms of hydrogen to ψ-cryptopine chloride and elimination of hydrogen chloride, a

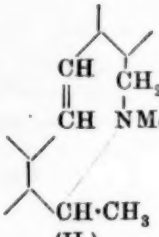
* In the reduction of *iso*cryptopine chloride, much *iso*dihydrocryptopine β-chloride is always obtained by the direct reduction of the ethenoid linking (p. 721), but the corresponding *iso*dihydro-ψ-cryptopine chloride does not appear to be one of the products of the reduction of ψ-cryptopine chloride Still more striking is the observation that, whereas during the reduction of *iso*cryptopine chloride, the base formed in much the larger quantity is tetrahydroanhydro*iso*cryptopine, $C_{21}H_{25}O_4N$, in the case of ψ-cryptopine chloride the reduction does not appear to proceed beyond the formation of the base $C_{21}H_{23}O_4N$ (m. p. 112°).

process which might take place in two different directions, leading to the formulæ



(I.)

and



(II.)

Judging from the course the reduction takes in the analogous case of *iso*cryptopine chloride, the new base should correspond in constitution with dihydroanhydro*iso*cryptopine (m. p. 195°, p. 722), that is to say, it should have the constitution represented by the partial formula I.

The investigation of the base has, however, shown that this is not the case. It does not, for example, yield 5 : 6-methylenedioxy-*o*-toluic acid, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H$ (p. 721), on oxidation with permanganate, and it can therefore scarcely contain the grouping, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CH{:}$, which is present in I. The alternative is that its constitution is that represented by formula II, and for this reason the base, $C_{21}H_{23}O_4N$, melting at 112°, has been named *ψ-anhydrodihydrocryptopine* (*A*) to indicate its relationship to anhydrodihydrocryptopine (*A*) (841). This base combines readily with methyl sulphate, and both the methosulphate,

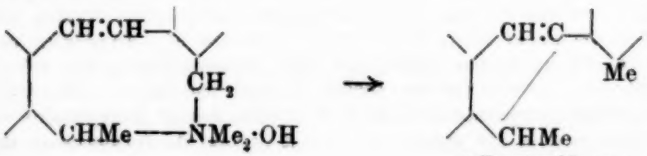
$$C_{21}H_{23}O_4N,Me_2SO_4,$$

and the corresponding methiodide, $C_{21}H_{23}O_4N,MeI$, are beautifully crystalline substances characterised by yielding highly coloured products on decomposition with methyl-alcoholic potassium hydroxide, which are obviously of complex nature and have not been further investigated.

When, however, the alkaline solution of the methosulphate is reduced by sodium amalgam, a remarkable change takes place, and a neutral substance, $C_{20}H_{20}O_4$, separates:

$$C_{20}H_{20}O_4NMe_2{\cdot}OH + 2H = C_{20}H_{20}O_4 + NHMe_2 + H_2O.$$

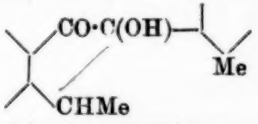
It is probable that this curious decomposition takes place in the following direction:



ψ-Cryptopidene.

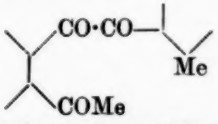
and, since the new substance, which crystallises beautifully and melts at 144°, is isomeric with cryptopidene (926; compare p. 772), it has been named *ψ-cryptopidene*.

An attempt was made to establish the constitution of the substance by studying its behaviour on oxidation with permanganate, but with partial success only. One of the substances produced is 5:6-methylenedioxy-*o*-toluic acid, the formation of which is in harmony with the suggested constitution. The principal products of oxidation are, however, *dioxy-ψ-cryptopidene*, $C_{20}H_{18}O_6$ (m. p. 138—140°), and *trioxy-ψ-cryptopidene*, $C_{20}H_{18}O_7$ (m. p. 165°). Both these substances exhibit a reaction reminiscent of the benzil reaction, that is to say, on boiling with methyl-alcoholic potassium hydroxide they dissolve to brown solutions which, in contact with air, become pink and gradually fade; the addition of hydrochloric acid then causes the precipitation of crystalline acids. Dioxy-ψ-cryptopidene yields a *semicarbazone*, $C_{21}H_{21}O_6N_3$, and trioxy-cryptopidene a *disemicarbazone*, $C_{22}H_{24}O_7N_6$, so that if the formula assigned to ψ-cryptopidene is correct, it is probable that these oxidation products may have the partial formulæ



Dioxy-ψ-cryptopidene.

and



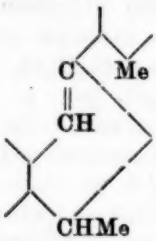
Trioxy-ψ-cryptopidene.

Section IV (b). *The Reduction of ψ-Cryptopine Chloride in Acid Solution* (p. 774).—It has just been explained that the methosulphate of ψ-anhydrodihydrocryptopine (*A*) undergoes a curious decomposition when it is reduced in alkaline solution, with loss of the nitrogen atom as dimethylamine and formation of a neutral substance, $C_{20}H_{20}O_4$ (ψ-cryptopidene).

It is perhaps still more remarkable that ψ-cryptopine chloride itself should, on reduction in acid solution with sodium amalgam, undergo a partial change in a similar direction, with elimination of the nitrogen atom, evidently as methylamine, and separation of a beautifully crystalline substance, $C_{20}H_{20}O_4$, which is isomeric with ψ-cryptopidene (m. p. 144°), melts at 152°, and has been named iso-*ψ-cryptopidene*. Since the melting points of the two substances do not greatly differ, it was at first thought that *iso*-ψ-cryptopidene might possibly be ψ-cryptopidene in a very pure condition; but this is not the case, because the mixture of the two substances melts at about 130°. On oxidation with permanganate, *iso*-ψ-cryptopidene yields considerable quantities of 5:6-methylenedioxy-*o*-tolualdehyde (m. p. 72—74°), as well as of the corresponding acid (m. p. 216°; compare p. 777), and also a substance,

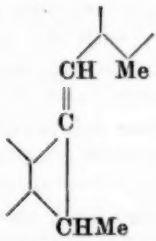
$C_{20}H_{20}O_5$ (*ketodihydroiso-ψ-cryptopidene*), which melts at 135° and yields a *semicarbazone*, $C_{21}H_{23}O_5N_3$.

The isomerism of ψ-cryptopidene and *iso*-ψ-cryptopidene is difficult to understand, but, as both yield 5:6-methylenedioxy-*o*-toluic acid on oxidation, it is suggested that the relationship may be that indicated by the formulæ



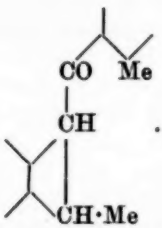
ψ-Cryptopidene.

and

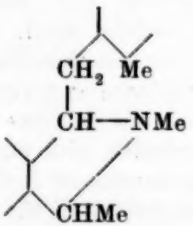


iso-ψ-Cryptopidene.

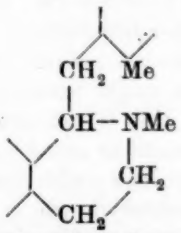
and it is probable that ketodihydro*iso*-ψ-cryptopidene contains the grouping:



The main product of the reduction of ψ-cryptopine chloride, in acid solution, is a base, $C_{21}H_{25}O_4N$, which is amorphous, but yields a crystalline picrate. Since this base gives 5:6-methylenedioxy-*o*-toluic acid on oxidation with permanganate, it is obvious that its constitution must be represented by the partial formula I, and it has therefore been named *dihydroanhydro-ψ-cryptopine*. The formation of this base is completely analogous to the conversion of *iso*cryptopine chloride into tetrahydroanhydro*iso*cryptopine (m. p. 138°, p. 722), and the similarity in constitution is clearly exhibited when the partial formulæ are compared:



Dihydroanhydro-ψ-cryptopine.



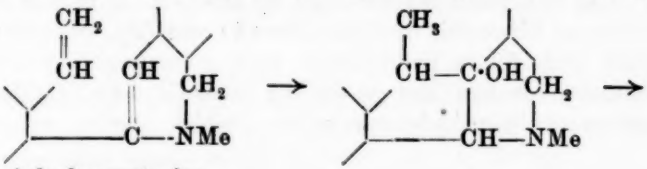
Tetrahydroanhydro*iso*cryptopine.

Section IV (c). *The Reduction of ψ-Methylberberinium Chloride* (p. 778).—In a communication published a short time ago (T., 1918, **113**, 750), it was shown that anhydroberberine methosulphate is converted by the action of hydrochloric acid into a substance called ψ-methylberberinium chloride, which is the analogue in the berberine series of ψ-cryptopine chloride. Since the latter substance exhibits the abnormal behaviour just described when reduced by sodium amalgam in acid solution, it was thought that it would be interesting to investigate the behaviour of ψ-methylberberinium chloride in the same circumstances. The strongly acid solution of ψ-methylberberinium chloride was therefore placed on sodium amalgam, when a neutral substance, $C_{20}H_{20}O_4$ (iso-ψ-*berberidene*), separated, which melts at 117° and exhibits the closest resemblance to *iso*-ψ-cryptopidene. The main product of the reduction was, however, again a base, $C_{21}H_{25}O_4N$ (*dihydroanhydro-ψ-methylberberine*), which, although amorphous, yields a crystalline picrate and hydriodide, and obviously corresponds with the amorphous base—dihydroanhydro-ψ-cryptopine—produced during the reduction of ψ-cryptopine chloride in acid solution.

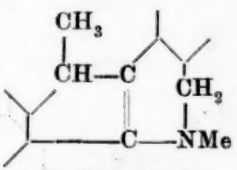
Section V.

iso*Anhydrocryptopine.*

*iso*Anhydrocryptopine is obtained from anhydrocryptopine by boiling with dilute hydrochloric acid, thus converting it into the isomeric hydroxy*iso*anhydrodihydrocryptopines, and then removing water from the latter by means of phosphoryl chloride (862).



Anhydrocryptopine.



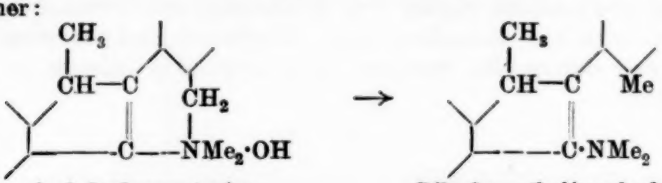
*iso*Anhydrocryptopine.

Anhydrocryptopine and *iso*anhydrocryptopine are obviously closely related, since both contain an unsaturated dihydro*iso*quinoline ring methylated at the nitrogen atom. The behaviour of this ring on reduction has been exhaustively studied in the case

of anhydrocryptopine methosulphate (p. 716), with unexpected results, and it seemed possible that additional information of importance might be obtained if the behaviour of *iso*anhydrocryptopine methosulphate were studied under similar conditions.

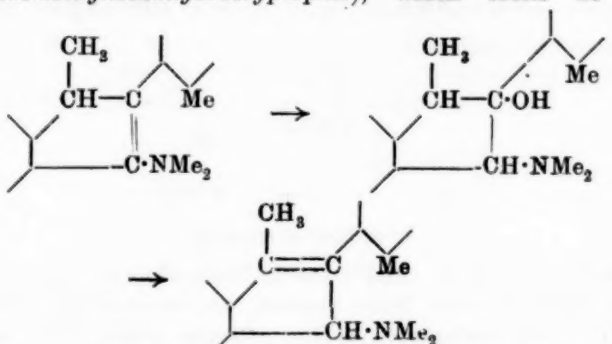
To some extent, this expectation was realised, but, on the other hand, wide differences, difficult to understand, were found to occur when the behaviour of the products of reduction obtained in the parallel cases to the subsequent action of reducing agents was investigated.

Section V (a). *The Reduction of* iso*Anhydrocryptopine Methosulphate in Alkaline Solution* (p. 782).—This methosulphate is readily reduced at the temperature of the steam-bath, when sodium amalgam acts on its aqueous solution, with the separation of a base, $C_{22}H_{25}O_4N$, which has been named *dihydromethyliso**anhydrocryptopine*. The examination of this base and its derivatives leaves little doubt that its formation is correctly represented in the following manner:



*iso*Anhydrocryptopine methohydroxide. Dihydromethyl*iso*anhydrocryptopine.

that is to say, it is formed by a process which is analogous to that which occurs when anhydrocryptopine methosulphate is reduced to dihydroanhydromethylcryptopine (p. 716). The new base melts at 122°, and is further characterised by the fact (i) that it exists in well-defined dimorphic modifications (*A*) and (*B*), and (ii) that, on boiling with dilute hydrochloric acid, it undergoes a curious intramolecular change and yields an isomeric base, $C_{22}H_{25}O_4N$ (*ψ-dihydromethyliso**anhydrocryptopine*), which melts at 140°.



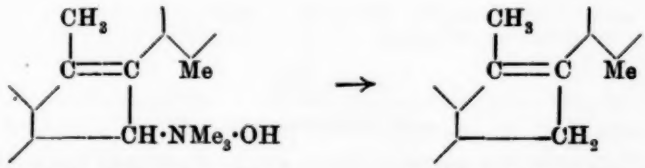
ψ-Dihydromethyl*iso*anhydrocryptopine.

This change is probably due to the addition and subsequent elimination of water, and it is suggested that the process takes place according to the scheme on p. 732.

The occurrence of the grouping, $\cdot CMe{:}C<$, receives support from the observation that ψ-dihydromethyl*iso*anhydrocryptopine is oxidised with unusual difficulty and resists the action of reducing agents in a remarkable degree (p. 788).

The most extraordinary change observed both in the case of dihydromethyl*iso*anhydrocryptopine and its ψ-isomeride is the behaviour of their methosulphates on reduction in alkaline solution by sodium amalgam.

In both cases, trimethylamine is eliminated with great ease, even at the ordinary temperature, and neutral substances, $C_{20}H_{20}O_4$, are produced which are isomeric with and somewhat similar in properties to cryptopidene and the ψ-cryptopidenes (compare pp. 718, 730). Under these conditions, the methosulphate of ψ-dihydromethyl*iso*anhydrocryptopine (m. p. 140°) yields, so far as could be ascertained, a single substance—iso*cryptopidene* (*A*)—melting at 167°, and there is reason to believe that this is formed according to the scheme:



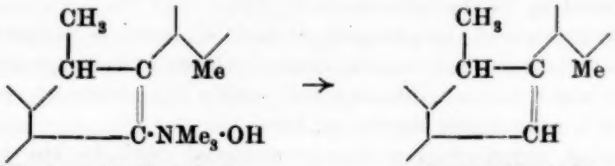
ψ-Dihydromethyl*iso*anhydrocryptopine methohydroxide.

*iso*Cryptopidene (*A*). (M. p. 167°.)

Dihydromethyl*iso*anhydrocryptopine methosulphate behaves in a different manner, yielding two substances, $C_{20}H_{20}O_4$, according to the conditions under which the reduction is carried out. If the aqueous solution of the methosulphate is reduced by sodium amalgam at 30°, decomposition takes place very gradually, and the neutral substance which separates melts at 167°, and is identical with the *iso*cryptopidene (*A*) obtained by the reduction of the methosulphate of the ψ-isomeride. The boiling aqueous solution of the methosulphate of dihydromethyl*iso*anhydrocryptopine is, however, very rapidly decomposed by crushed sodium amalgam, the neutral substance, $C_{20}H_{20}O_4$, produced melts at 108°, and is therefore isomeric with *iso*cryptopidene (*A*). It has been named iso*cryptopidene* (*B*).

If an attempt is made to explain this puzzling state of things, it

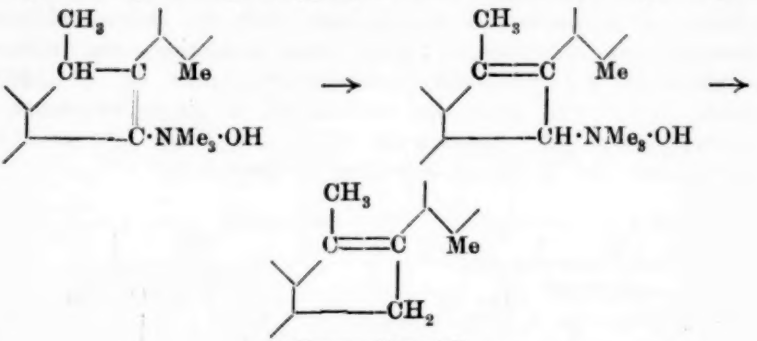
may be suggested that the rapid formation of the substance melting at 108° is the direct process,



Dihydromethyl*iso*anhydrocryptopine methohydroxide.

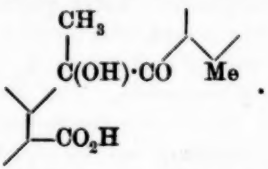
*iso*Cryptopidene (*B*). (M. p. 108°.)

and that during the slow process at 30° the prolonged action of the alkali causes addition and subsequent elimination of water in the direction which is assumed to take place during the conversion of dihydromethyl*iso*anhydrocryptopine into its ψ-isomeride (p. 732).



*iso*Cryptopidene (*A*).

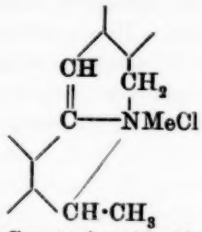
It is, however, obvious that the changes which take place during these eliminations of trimethylamine are most unusual, and explanations of the course which these decompositions take must therefore be considered as merely provisional. Some confirmation of the constitution assigned to *iso*cryptopidene (*B*) is to be found in its behaviour on oxidation, when it yields a new acid, $C_{20}H_{20}O_8$ (m. p. 227°), which has been named *ketohydroxydihydroisocryptopidenic acid*, and very probably has the constitution



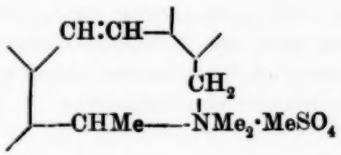
An acid of this constitution could scarcely result from the oxidation of *iso*cryptopidene (*A*) if the formula assigned to this substance above is correct.

One of the most remarkable decompositions which have been

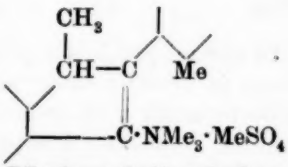
observed during the course of this long investigation is the process of reduction by sodium amalgam, sometimes in alkaline and sometimes in acid solution, which results in the elimination of the nitrogen atom and separation of a neutral substance, $C_{20}H_{20}O_4$. This change has been observed in the following cases:



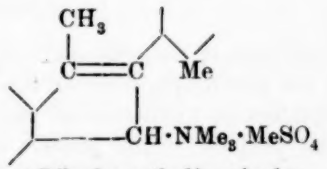
ψ-Cryptopine chloride and ψ-methylberberinium chloride.
(I.)



ψ-Anhydrodihydrocryptopine (*A*) methosulphate.
(II.)

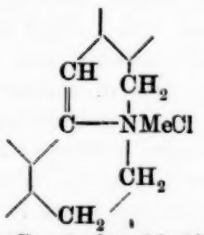


Dihydromethyl*iso*anhydrocryptopine methosulphate.
(III.)

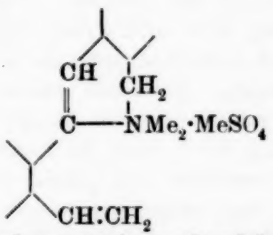


ψ-Dihydromethyl*iso*anhydrocryptopine methosulphate.
(IV.)

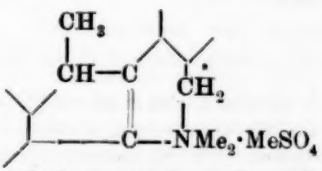
and the nitrogen atom is eliminated as methylamine in (I), as dimethylamine in (II), and as trimethylamine in (III) and (IV). On the other hand, substances very similar in constitution to those figured above, such, for example, as



*iso*Cryptopine chloride.



Anhydrocryptopine methosulphate.



*iso*Anhydrocryptopine methosulphate.

do not lose the nitrogen atom when subjected to the action of sodium amalgam under the same conditions.

This matter is obviously very complex and difficult to understand, and, at the present stage, is seems impossible to form any idea as to the conditions which cause the nitrogen atom to be in so reactive a state that it is readily removed by the action of sodium amalgam, sometimes at the ordinary temperature. If opportunity occurs, it is proposed to study the mechanism of changes of this kind in the case of *iso*quinoline derivatives and other analogous substances of less complex structure than the substances discussed in the present communication.

Experimental.

Preparation of Anhydrocryptopine Methosulphate, $C_{21}H_{21}O_4N,Me_2SO_4$.

It has already been pointed out that the process previously given (978) for the preparation of this substance is unsatisfactory, and, as considerable quantities of this valuable material were required for the purpose of the present investigation, comparative experiments were instituted, and finally the following conditions were found to give a yield of more than 80 per cent. of that theoretically possible.

The anhydrocryptopine employed was prepared from *iso*cryptopine chloride substantially according to the method already described (975), but it is not necessary to use more than 20 c.c. of 25 per cent. methyl-alcoholic potassium hydroxide for each 10 grams of the chloride. The product was washed thoroughly at the pump, first with water, then several times with methyl alcohol, in which anhydrocryptopine is very sparingly soluble, and finally with water. The pale yellow product was left in contact with porous porcelain until air-dry, then dried at a temperature not exceeding 80°* until no further loss in weight occurred; finally, it was powdered and passed through a very fine sieve. Prepared in this way, anhydrocryptopine is nearly pure and melts at about 108—110°; it contains, at the most, traces of inorganic matter and of *iso*cryptopine chloride.

In order to prepare the methosulphate, anhydrocryptopine (10 grams) is shaken in a corked flask with excess of freshly distilled

* If the temperature is allowed to rise to 95—100°, the mass soon becomes brown and viscid and rapidly decomposes, a change which appears to be mainly the result of oxidation. For the successful preparation of the methosulphate, anhydrocryptopine must be quite dry.

methyl sulphate (10 c.c.), when a paste is formed and there is no apparent immediate action. On keeping, the paste rapidly thickens, and in two days will have set to a hard cake. After remaining for four days, the flask is broken, and the cake crushed and washed at the pump with benzene, which removes the excess of methyl sulphate and colouring matter.*

The dry, pale yellow residue is left on porous porcelain until the adherent benzene has evaporated; it then weighs 11 grams, and is dissolved in boiling methyl alcohol, from which the pure methosulphate separates, on slowly cooling, in brilliant sulphur-yellow prisms, and melts at 238—240°, as previously stated. The measurement of some fine crystals of anhydrocryptopine methosulphate was kindly undertaken by Miss M. Porter, with the following result:

The crystals are monoclinic with axial ratios $a:b:c=1{\cdot}504:1:0{\cdot}931$, $\beta=104°15'$, the forms observed being $a\{100\}$, $m\{110\}$, $c\{001\}$, $r\{\bar{1}01\}$, and $e\{102\}$. The habit is tabular parallel to $c(001)$, and very much elongated along the b-axis, as shown in Fig. 1. The form $c\{001\}$ is the predominant terminating form; $r\{\bar{1}01\}$ is well developed, and $e\{102\}$, when present, is very narrow. The crystals gave poor reflections; three were measured, and the results are placed in the table below.

	No. of read-	Azimuth (ϕ).			Polar distance (ρ).		
Face.	ings.	Limits.	Obs.	Calc.	Limits.	Obs.	Calc.
a (100)	4	89°55′—90° 5′	90° 1′	90°0′	90° 0′—90° 0′	90° 0′	90° 0′
m (110)	4	34 30 —34 42	*34 34	—	90 0 —90 0	90 0	90 0
c (001)	3	87 25 —90 35	88 47	90 0	15 48 —16 2	*15 15	—
r ($\bar{1}$01)	3	87 45 —90 15	89 33	90 0	19 53 —20 30	*20 15	—
e (102)	1	—	90 41	90 0	—	30 30	30 40

Determinants: 010/001/100. Complex-symbol: 4h; $-15/64\frac{1}{2}/+2$.

FIG. 1.

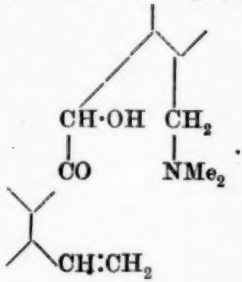
* A quicker process is to dissolve the cake in boiling methyl alcohol, from which the methosulphate separates, on cooling, in an almost pure condition. The yield, however, is not so good as that obtained after extraction with benzene. This is probably due to the fact that the solution in boiling methyl alcohol, containing the excess of methyl sulphate, rapidly becomes very acid, and this causes some decomposition of the methosulphate.

The methyl-alcoholic mother liquors of the pure methosulphate yielded, on concentrating, a further crop of less pure methosulphate, and, on concentrating further and leaving in the ice-chest, a mass of soft, yellow, nearly square plates separated, together with a few of the large prisms of the methosulphate. The two substances were easily separated by means of a sieve, and the second substance, after recrystallisation from water, proved to be *anhydrocryptopine methyl hydrogen sulphate*:

0·1181 gave 0·2471 CO_2 and 0·0582 H_2O. C=57·2; H=5·5.
$C_{21}H_{21}O_4N,MeHSO_4$ requires C=57·0; H=5·4 per cent.

The most striking difference between the methosulphate and this salt lies in the fact that, whereas the solution of the former gives no precipitate with ammonia, the addition of ammonia to that of the latter causes the immediate separation of a caseous precipitate which, after crystallisation from methyl alcohol, melts at 110—111°, and consists of anhydrocryptopine.

Oxidation of Anhydrocryptopine Methochloride to Dioxymethyl-



*iso**anhydrodihydrocryptopine*** (945),

This oxidation was carried out by dissolving anhydrocryptopine methochloride (5 grams; compare 981) in water (1 litre), and, after cooling in ice and salt until the solution was partly frozen, cold saturated permanganate (containing 5·5 grams of $KMnO_4$) was gradually added with mechanical stirring. The permanganate was immediately decolorised, and, when the operation was complete, the whole was heated to boiling, filtered, and the brown filtrate concentrated to half its bulk, during which a small quantity of a crystalline substance separated. After two days, this was collected (0·5 gram), and a second small quantity was obtained by further concentrating the deep brown filtrate, the total yield being 0·67 gram. On still further concentrating, the odour of dimethylamine became apparent, and all attempts to obtain anything crystalline from the tar which resulted were unsuccessful. The crystalline substance (0·67 gram) is sparingly soluble in cold

alcohol and not very readily so on boiling, and separates in drab needles. After twice recrystallising, the following analytical details were obtained with different preparations:

0·1129 gave 0·2724 CO_2 and 0·0633 H_2O. C = 65·8; H = 6·2.
0·1026 „ 0·2496 CO_2 „ 0·0596 H_2O. C = 66·3; H = 6·4.

$C_{22}H_{25}O_6N$ requires C = 66·2; H = 6·3 per cent.

Dioxymethylisoanhydrodihydrocryptopine melts at 187—188°, and is sparingly soluble in benzene or acetone in the cold and nearly insoluble in light petroleum. It dissolves in boiling acetone and separates in glistening balls of needles. The substance is a strong base, dissolves immediately in cold dilute hydrochloric acid, and gives, on the addition of ammonia, a milky liquid and an amorphous precipitate which, on warming, becomes crystalline. The sulphate and nitrate, like the hydrochloride, are readily soluble. The addition of platinic chloride to the dilute solution of the hydrochloride produces an ochreous precipitate, which melts to a green oil under boiling water, and the supernatant liquid becomes first green and then brown. Auric chloride produces, with a dilute solution of the hydrochloride, a pale chocolate precipitate, soluble in hot water, and, on boiling, the liquid becomes green and deposits a purple precipitate of reduced gold. When a few drops of copper sulphate are added to the solution of the hydrochloride, a pale yellowish-green solution is obtained which, on boiling, becomes first deep blue, then yellow, and finally deep reddish-brown; the addition of alkali then precipitates a reddish-brown precipitate of cuprous oxide.

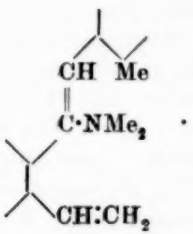
The solution of the base in ordinary dilute nitric acid becomes deep green when heated at about 80°, and is dichroic with a red reflex; if the temperature is raised to the boiling point, the intense colour suddenly changes to pale brown, and the odour of nitrous acid develops.

When concentrated nitric acid is poured on to a trace of the substance on a watch-glass, a brilliant orange-red colour is produced, which soon becomes crimson, and then the addition of water gives a crimson solution, which fades to yellow. The solution of the base in glacial acetic acid gives no immediate coloration on the addition of sulphuric acid, but gradually a pink colour develops. If the base is mixed with acetyl chloride in a sealed tube, it becomes crimson, then violet, and finally intense indigo-blue, and, on heating in boiling water, the colour changes to deep green. The whole dissolves completely in water to a brown solution, and ammonia precipitates a chocolate, gelatinous substance which dries to a chocolate-black powder The base does not exhibit the characteristic purple benzoin reaction when it is warmed with

dilute sodium hydroxide or boiled with methyl-alcoholic potassium hydroxide, but, in the latter case, it is converted into a white substance, which is apparently a potassium derivative, and this is decomposed by water with the separation of a white, flocculent precipitate.

The base appears to yield a semicarbazone when it is boiled with excess of semicarbazide hydrochloride and sodium acetate and the product precipitated with ammonia, but the amount of available material was too small for purification and analysis.

Section I (a). *Reduction of Anhydrocryptopine Methosulphate in Alkaline Solution: Formation of Dihydroanhydromethylcryptopine,*



Dihydroanhydromethylcryptopine is obtained when anhydrocryptopine methosulphate is reduced in alkaline solution by sodium amalgam under the following conditions: The methosulphate (10 grams), dissolved in boiling water (200 c.c.), was poured on crushed sodium amalgam (100 grams of 4 per cent.) in a porcelain beaker, and the whole vigorously stirred, when a base at once separated which adhered to the sides of the beaker and to the glass rod, and hardened on cooling. The mass was ground up, well washed, dissolved in boiling methyl alcohol, the filtered solution mixed with ether, and the methyl alcohol removed by washing with water. After drying over potassium carbonate, the ethereal solution was concentrated and left for several days in the ice-chest, but, as no crystallisation took place, the ether was evaporated. The hard residue, which resembled colophony, was dissolved in dilute hydrochloric acid and mixed with ammonia, when an amorphous base separated, which was dried over phosphoric oxide in a vacuum desiccator. Two different preparations were analysed:

0·1055 gave 0·2758 CO_2 and 0·0619 H_2O. C = 71·3; H = 6·5.
0·1255 „ 0·3312 CO_2 „ 0·0764 H_2O. C = 71·9; H = 6·8.
$C_{22}H_{25}O_4N$ requires C = 71·9; H = 6·8 per cent.

Dihydroanhydromethylcryptopine exhibits no tendency to crystallise; its solution in acetic acid gives with sulphuric acid a port

wine coloration, which changes to deep brown on the addition of a drop of dilute nitric acid. The salts are readily soluble, and the solution of the hydrochloride gives, on the addition of potassium iodide, a viscid iodide which dissolves readily in methyl alcohol, but could not be obtained crystalline. The *platinichloride*, prepared by the addition of platinic chloride to the dilute solution of the hydrochloride, is a pale ochreous, chalky precipitate:

0·1265 gave 0·2146 CO_2 and 0·0516 H_2O. C=46·2; H=4·5.
$(C_{22}H_{25}O_4N)_2H_2PtCl_6$ requires C=46·2; H=4·5 per cent.

Oxidation of Dihydroanhydromethylcryptopine.—In order to obtain evidence as to the constitution of this base, the substance (5 grams), dissolved in acetone, was oxidised by the gradual addition of finely powdered permanganate (5·5 grams) at the ordinary temperature. The product was filtered, the manganese precipitate (*A*) well washed with acetone, the filtrate evaporated, and the brown syrup, which had a distinct odour of piperonal, distilled in a current of steam. The cloudy distillate deposited, on keeping in the ice-chest, a large crop of needles which melted at 70—72°, and were recognised as 5:6-methylenedioxy-*o*-tolualdehyde (907).

The residue in the steam distillation flask contained an oil, most of which was soluble in dilute hydrochloric acid, but no further examination was made. The manganese precipitate (*A*) yielded, on extraction with boiling water, a brown solution, which was digested with animal charcoal, concentrated, and acidified, when a solid acid separated and crystallised from glacial acetic acid in colourless needles, melted at 214—216°, and consisted of 5:6-methylenedioxy-*o*-toluic acid (916).

Dihydroanhydromethylcryptopine Methosulphate, $C_{22}H_{25}O_4N,Me_2SO_4$.

The solution of the base (3 grams) in benzene (15 c.c.) reacts readily with methyl sulphate (3 c.c.), with development of heat, and in a short time the methosulphate separates as a crystalline mass. This was collected, washed with benzene, and crystallised from water, in which it is rather sparingly soluble in the cold, but readily so on boiling, and from which it separates in colourless groups of prisms:

0·1164 gave 0·2499 CO_2 and 0·0661 H_2O. C=58·5; H=6·3.
$C_{22}H_{25}O_4N,Me_2SO_4$ requires C=58·4; H=6·3 per cent.

This methosulphate melts at 210°, without effervescence, to a slightly coloured syrup; the solution in acetic acid gives with sulphuric acid a deep cherry-red coloration which, on the addition

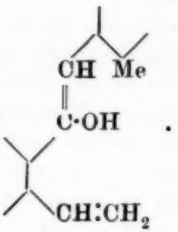
of a drop of dilute nitric acid, changes to brownish-violet. The corresponding *methiodide*, $C_{22}H_{25}O_4N,MeI$, is obtained by adding hot dilute potassium iodide to the hot dilute solution of the methosulphate, when a milky liquid is produced, which soon deposits glistening spangles:

0·1123 gave 0·2242 CO_2 and 0·0559 H_2O. C=54·4; H=5·5.

$C_{22}H_{25}O_4N,MeI$ requires C=54·2; H=5·5 per cent.

This iodide is remarkably stable, it scarcely darkens at 200°, and melts at about 217° with very little decomposition.

Hydroxycryptopidene (compare 926),



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This interesting substance, isomeric and closely allied in properties with *α-iso*cryptopidol (m. p. 90—92°; 948), is obtained when dihydroanhydromethylcryptopine methosulphate is decomposed by methyl-alcoholic potassium hydroxide. The methosulphate (7 grams), dissolved in hot methyl alcohol, was mixed with methyl-alcoholic potassium hydroxide (60 c.c. of 25 per cent.) and heated to boiling, when trimethylamine was immediately eliminated, but decomposition was nevertheless slow.

After an hour, most of the methyl alcohol was evaporated, and the pasty residue heated in boiling water for two hours; water was then added, and the viscid precipitate extracted with much ether. The ethereal solution, which contained a flocculent precipitate consisting apparently of a polymeric modification of hydroxycryptopidene (compare below), was filtered, thoroughly washed with dilute hydrochloric acid, dried over potassium carbonate, and concentrated, when, on remaining for several days in the ice-chest, a crust of nodules separated which melted at 88—89°, and consisted of pure hydroxycryptopidene. As the amount which had separated was only small, the ethereal mother liquor was evaporated, when a pale brown syrup remained which soon began to crystallise in nodules, and crystallisation was much facilitated by trituration with methyl alcohol, in which the substance is sparingly soluble. After collecting and washing with methyl alcohol, the colourless residue was recrystallised from methyl alcohol, from which hydroxycryptopidene separates in circular nodules melting at 87—89°. Two different preparations were analysed:

0·1272 gave 0·3288 CO_2 and 0·0704 H_2O. C=70·4; H=6·1.
0·1289 „ 0·3336 CO_2 „ 0·0701 H_2O. C=70·5; H=6·1.
$C_{20}H_{20}O_5$ requires C=70·6; H=5·9 per cent.

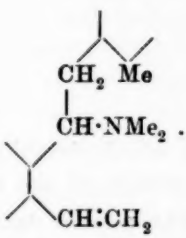
Hydroxycryptopidene is very readily soluble in benzene, but sparingly so in ether or cold, light petroleum. It dissolves, however, moderately readily in the latter solvent on boiling, and separates in well-developed chisel-shaped prisms and also in single lenticular prisms.

Hydroxycryptopidene dissolves in acetyl chloride in the cold with some development of heat, and, when heated in a sealed tube, the solution becomes purple, then bluish-violet, and finally deep indigo-blue. When the product is evaporated on the steam-bath, a blue resin remains, which loses its colour on boiling with methyl alcohol, and a chalky substance separates. This was collected, washed with methyl alcohol, in which it is nearly insoluble, and purified by dissolving in glacial acetic acid and precipitating with methyl alcohol. After washing with methyl alcohol, the chalky residue contained 4·98 per cent. of chlorine, and this was removed by boiling with 10 per cent. methyl-alcoholic potassium hydroxide. The precipitate was then collected, washed well with methyl alcohol, then with water, dissolved in glacial acetic acid, and precipitated by methyl alcohol:

0·1158 gave 0·3005 CO_2 and 0·0603 H_2O. C=70·8; H=5·8.
$C_{20}H_{20}O_5$ requires C=70·6; H=5·9 per cent.

Clearly the action of the acetyl chloride had been, not to produce an acetyl derivative, but to convert the hydroxycryptopidene into a polymeric modification, which, since it closely resembles *β-iso*cryptopidol (947), may be named *hydroxy*isocryptopidene (*β*). This polymeride shrinks at 175—180° and froths up at about 200°.

Section I (b). *Reduction of Anhydrocryptopine Methosulphate in Acid Solution: Formation of Tetrahydroanhydromethylcryptopine,*



In preparing tetrahydroanhydromethylcryptopine, anhydrocryptopine methosulphate (5 grams), dissolved in warm water

(100 c.c.) and dilute hydrochloric acid (5 c.c.), was poured on sodium amalgam in a flat basin, and then hydrochloric acid (20 c.c.) gradually added, so that the whole always remained distinctly acid.* As soon as the amalgam was exhausted, the liquid was filtered from a small quantity of a viscid substance insoluble in dilute hydrochloric acid, mixed with excess of ammonia, and the milky product extracted with ether. The ethereal solution was washed with water, dried over potassium carbonate, and concentrated, and, as no crystallisation had taken place after remaining for a week in the ice-chest, the ether was evaporated. The gummy residue was then dissolved in dilute hydrochloric acid, precipitated by ammonia, and, after collecting and washing, the base was dried in a vacuum desiccator over phosphoric oxide:

0·1140 gave 0·2972 CO_2 and 0·0757 H_2O. C=71·1; H=7·4.

$C_{22}H_{27}O_4N$ requires C=71·5; H=7·3 per cent.

Tetrahydroanhydromethylcryptopine, isomeric with anhydrotetrahydromethylcryptopine (m. p. 107°; 898), has not been obtained in a crystalline condition.

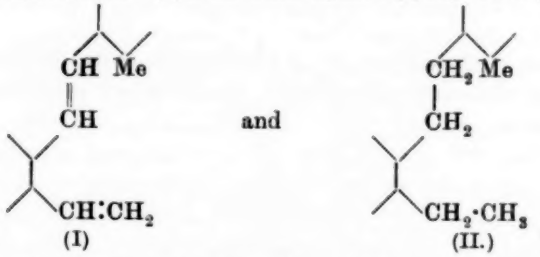
It is readily soluble in dilute hydrochloric acid, and the addition of concentrated hydrochloric acid produces a milky liquid, from which the hydrochloride separates as a syrup. The *platinichloride*, prepared in the usual manner, is an ochreous precipitate somewhat soluble in hot water, from which it separates as a chalky powder:

0·1175 gave 0·1997 CO_2 and 0·0539 H_2O. C=46·3; H=5·0.

0·4372 „ 0·0719 Pt. Pt=16·4.

$(C_{22}H_{27}O_4N)_2,H_2PtCl_6$ requires C=46·1; H=5·0; Pt=16·9 per cent.

Cryptopidene (I) *and Tetrahydrocryptopidene* (II),



(I) (II.)

The methosulphate of tetrahydroanhydromethylcryptopine does not separate when the solution of the base (2 grams) in benzene

* It is important that the temperature should not rise above 60°, and that a large excess of hydrochloric acid is not present at any time, otherwise there is a risk of the formation of considerable quantities of ψ-cryptopine chloride (compare p. 767).

(5 c.c.) is mixed with methyl sulphate (2 c.c.) and allowed to remain for twenty-four hours.

On the addition of ether, the methosulphate is deposited, however, as a syrup, which on rubbing shows signs of crystallising. The syrup was washed with ether, dissolved in a little methyl alcohol, and boiled with methyl-alcoholic potassium hydroxide (20 c.c. of 30 per cent.), when trimethylamine was eliminated, and, after half an hour, the methyl alcohol was evaporated, the residue mixed with water, and extracted with ether. The ethereal solution, which had a lilac fluorescence, after well washing with dilute hydrochloric acid and drying over potassium carbonate, deposited on evaporation a syrup, which soon crystallised, and contact with porous porcelain removed traces of oily impurity. The colourless residue separated from methyl alcohol in glistening needles exhibiting a striking lilac fluorescence, melted at 122—123°, and was recognised as *cryptopidene*. The identity was confirmed by analysis (Found: C = 73·6; H = 6·2. $C_{20}H_{20}O_4$ requires C = 74·1; H = 6·2 per cent.) and by the fact that the mixture with a specimen of cryptopidene which had previously been obtained from anhydrotetrahydromethylcryptopine methosulphate (926) melted at 120—122°.

Tetrahydrocryptopidene, $C_{20}H_{24}O_4$.—This fine substance is obtained when cryptopidene is reduced in boiling alcoholic solution with sodium, but the change does not take place very readily and completely.

The boiling solution of cryptopidene (5 grams) in alcohol (100 c.c.) was run on to melted sodium (10 grams) contained in a flask fitted with a long condenser and heated in boiling salt solution. Small quantities of boiling alcohol were run in from time to time, and, so soon as all the sodium had dissolved, water was added, the whole extracted with ether, the ethereal solution washed thoroughly, dried, and evaporated, when a crystalline residue remained, which, however, contained unchanged cryptopidene. The reduction was twice repeated exactly as in the first instance, and the product repeatedly recrystallised from methyl alcohol, in which tetrahydrocryptopidene is rather sparingly soluble in the cold, and from which it separates in glistening groups of prisms exhibiting a lilac fluorescence. Considerable difficulty was experienced in obtaining accurate analytical results:

0·1236 gave 0·3284 CO_2 and 0·0797 H_2O. C = 72·6; H = 7·2.
0·1142 „ 0·3048 CO_2 „ 0·0750 H_2O. C = 72·7; H = 7·3.
$C_{20}H_{24}O_4$ requires C = 73·2; H = 7·3 per cent.

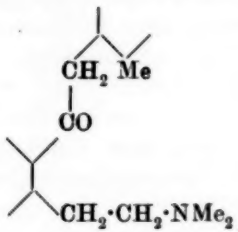
Tetrahydrocryptopidene melts at 78°, and is readily soluble in

hot alcohol, acetone, acetic acid, or benzene. It is sparingly soluble in light petroleum (b. p. 60—80°) in the cold, but dissolves readily on boiling, and separates splendidly in stout, well-developed tabular prisms with bevelled edges when the solution is allowed to cool very slowly or to concentrate spontaneously. The solution in acetic acid gives with sulphuric acid an orange-red coloration, which changes to a port wine colour on the addition of a drop of dilute nitric acid. It dissolves in concentrated nitric acid with a striking crimson colour, which soon fades.

Section II.

Reduction of Cryptopine Methochloride in Alkaline Solution.

Dihydromethylcryptopine,



In studying this reduction, the solution of the methochloride (881) (5 grams) in water (100 c.c.) was treated at about 50° with sodium amalgam (100 grams of 4 per cent.), when rapid separation of a viscid, grey base occurred, and the completion of the process was facilitated by heating on the steam-bath. The base was dissolved in methyl alcohol, mixed with much ether, the ethereal solution thoroughly washed with water, dried over potassium carbonate, and concentrated, when, on keeping in the ice-chest, a hard crust of rather indefinite crystals gradually separated, which melted at about 100—102°. The crystals were again dissolved in dry ether, by the aid of methyl alcohol as before, and the rather concentrated liquid then deposited a small quantity of glistening, prismatic needles (0·2 gram) of dihydromethylcryptopine, which became opaque on drying in the steam-oven:

0·1184 gave 0·2977 CO_2 and 0·0757 H_2O. C = 68·6; H = 7·1.

$C_{22}H_{27}O_5N$ requires C = 68·6; H = 7·0 per cent.

Dihydromethylcryptopine melts at 118—120°, and is readily soluble in hot methyl alcohol, but sparingly so in the cold, separating from the hot solution on slowly cooling in glistening, six-sided prisms. When triturated with dilute hydrochloric acid, the base at first becomes viscid, and then the very sparingly soluble hydrochloride forms, which dissolves in boiling dilute hydrochloric

acid and separates as a crust of microscopic prisms. The solution of a trace of the base in a drop of glacial acetic acid gives, with sulphuric acid, a deep reddish-brown coloration.

Oxidation.—The base (0·7 gram), dissolved in acetone (20 c.c.), was oxidised by the gradual addition of very finely powdered permanganate (1·2 grams), but the reduction of the permanganate took place unusually slowly and required two days for completion at the ordinary temperature.

After filtering and washing with acetone, the manganese precipitate was extracted with boiling water, the extract digested with animal charcoal, evaporated to a small bulk, and acidified, when a cloudy liquid was produced, which soon deposited a sparingly soluble, crystalline acid.

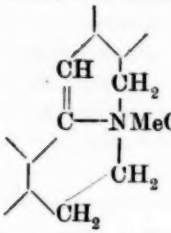
This was collected and recrystallised from glacial acetic acid, when it separated in colourless needles melting at 214—216°, which were recognised as 5:6-methylenedioxy-*o*-toluic acid,

$$CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H \ (916).$$

The acetone extract from the oxidation was scarcely coloured, and yielded, on evaporation, a syrup which had the odour of piperonal, and was largely insoluble in dilute hydrochloric acid. On distilling in a current of steam, there separated from the distillate needles which melted at 72—73°, and consisted of 5:6-methylenedioxy-*o*-tolualdehyde, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CHO$ (907).

The ethereal mother liquors from which the dihydromethylcryptopine had separated, as explained above, were concentrated and left for some days in the ice-chest; the hard cake of crystals was then dissolved in dilute hydrochloric acid, and again allowed to remain, when a crust of crystals (0·8 gram) of anhydrotetrahydromethylcryptopine hydrochloride, $C_{22}H_{27}O_4N,HCl$ (900), separated. This sparingly soluble hydrochloride was removed by filtration, the filtrate made strongly alkaline with ammonia, and the viscid base extracted with ether. After drying over potassium carbonate and concentrating, the ethereal solution deposited hard crystals which melted at 106—107°, and consisted of tetrahydromethylcryptopine, $C_{22}H_{29}O_5N$ (896). The latter is the principal product of the reduction of cryptopine methochloride under the conditions described at the beginning of this section. Experiments were also made on the reduction of cryptopine methosulphate (880) in alkaline solution with sodium amalgam, but the only product that could be isolated was tetrahydromethylcryptopine.

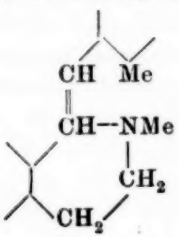
Section III (a). *The Reduction of* iso*Cryptopine Chloride,*



in Alkaline Solution.

For the purpose of this investigation, crushed sodium amalgam (100 grams of 4 per cent.) was added to *iso*cryptopine chloride (5 grams), dissolved in about 400 c.c. of boiling water, and the whole placed on the steam-bath and well stirred, the water being replaced as it evaporated.

A viscid base soon began to separate, and, after an hour, the whole was filtered hot and the residue washed with hot water. The filtrate, mixed with excess of hydrochloric acid, deposited a large quantity of a quaternary salt, which was readily recognised as *iso*dihydrocryptopine β-chloride (compare p. 721), and this substance is produced in such considerable amount that this process affords a much more convenient means for its preparation than that previously described (934). The viscid base was dissolved in alcohol and mixed with much ether, which caused a further small quantity of the quaternary salt to separate; this was filtered off, the ethereal solution washed thoroughly until free from alcohol, quickly dried over potassium carbonate, and filtered. During the subsequent concentration, a base began to separate on the sides of the flask as a glistening, crystalline crust, and, on long keeping in the ice-chest, this increased considerably. When this deposit was fractionally crystallised from methyl alcohol, it separated into (i) considerable quantities of *tetrahydroanhydroisocryptopine*, $C_{21}H_{25}O_4N$ (m. p. 138°), identical with the base obtained as one of the products of the reduction of *iso*cryptopine chloride in acid solution (p. 751), and quite small quantities of a new base, $C_{21}H_{23}O_4N$—*dihydroanhydroisocryptopine*—melting at 195°, the constitution of which is represented by the formula



0·0829 gave 0·2174 CO_2 and 0·0480 H_2O. C = 71·5; H = 6·4.
0·1246 „ 0·3261 CO_2 „ 0·0729 H_2O. C = 71·4; H = 6·5.
$C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·5 per cent.

This interesting substance separates from alcohol or methyl alcohol, in both of which it is very sparingly soluble, in pale lemon-yellow needles.

It is also sparingly soluble in boiling benzene or acetone, and separates particularly well from the latter in glistening needles. The solution in glacial acetic acid gives no coloration with sulphuric acid but, on the addition of a drop of dilute nitric acid, an intense permanganate coloration rapidly develops.

The Hydrochloride.—The base dissolves readily in dilute hydrochloric acid, and, on rubbing, the hydrochloride soon separates in needles. It is readily soluble in boiling water, but almost insoluble in dilute hydrochloric acid in the cold:

0·1151 gave 0·2721 CO_2 and 0·0652 H_2O. C = 64·5; H = 6·3.
$C_{21}H_{23}O_4N$,HCl requires C = 74·7; H = 6·2 per cent.

The sulphate is soluble and does not appear to crystallise readily, but the addition of nitric acid to the dilute solution of the sulphate immediately precipitates the nitrate, which is very sparingly soluble in hot dilute nitric acid and crystallises rather indefinitely. When boiling dilute potassium iodide is added to the boiling dilute solution of the sulphate, a milky liquid is produced, from which the *hydriodide* soon separates as a crystalline mass. This was collected and recrystallised from boiling alcohol, in which the salt is sparingly soluble and from which it separates in warty aggregates melting at about 250—255° with decomposition to a yellow froth:

0·1046 gave 0·2017 CO_2 and 0·0471 H_2O. C = 52·6; H = 5·0.
$C_{21}H_{23}O_4N$,HI requires C = 52·4; H = 5·0 per cent.

Section III (b). *The Reduction of* iso*Cryptopine Chloride in Acid Solution.*

In attempting this reduction, considerable difficulty was experienced owing to the sparing solubility of *iso*cryptopine chloride in dilute hydrochloric acid, and, indeed, in mineral acids in general.

Ultimately, however, the following process was found to work well.

*iso*Cryptopine chloride (5 grams), dissolved in glacial acetic acid (25 c.c.), is mixed with boiling water (100 c.c.), and, after heating to boiling, concentrated hydrochloric acid (20 c.c.) is added, and the whole poured on sodium amalgam (100 grams of 4 per

cent.) in an enamelled iron basin. So soon as the vigorous action has subsided, the same quantity of sodium amalgam is again added, as well as sufficient hydrochloric acid to keep the liquid strongly acid. The whole while hot is decanted from the mercury on to a Büchner funnel connected with the pump, and the filtrate, which immediately begins to crystallise in minute needles, left overnight.

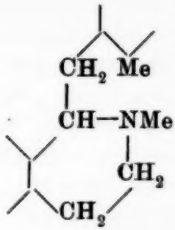
The precipitate (*A*) is collected, washed with a little water, the filtrate heated to boiling and mixed with excess of ammonia, when a viscid, grey mass (*B*) separates, which is immediately filtered off, and the filtrate, on keeping overnight, becomes filled with a soft mass of needles (*C*). The substance (*A*), which is almost pure *iso*cryptopine chloride, is again reduced as before, and, even after the operation has been repeated four times, *iso*cryptopine chloride still remains.

This was proved by analysis (Found: C = 59·3; H = 6·3. $C_{21}H_{22}O_4NCl,2H_2O$ requires C = 59·5; H = 6·1 per cent.) and also by the fact that the salt yielded anhydrocryptopine (975) on decomposition with methyl-alcoholic potassium hydroxide. The quaternary salt (*C*) crystallised well from hot dilute hydrochloric acid in long needles, and, in contact with porous porcelain, dried to a horny mass which did not melt at 260°. On examination, this salt was found to be *iso*dihydrocryptopine β-chloride, since, when digested with methyl-alcoholic potassium hydroxide, it yielded a substance which, after crystallisation from acetone, melted at 178°, and was recognised as anhydrodihydrocryptopine (*A*) (938).

The viscid, grey mass (*B*) hardens on keeping, and becomes crystalline in contact with methyl alcohol. The whole is dissolved in boiling methyl alcohol and set aside, when a crop of crystals separates which usually consists of a mixture of *tetrahydroanhydro*-iso*cryptopine* (m. p. 138°) and *dihydroanhydrodihydrocryptopine* (*A*) (m. p. 164°).

The latter of these is much the less soluble in methyl alcohol, and at some concentrations separates almost completely before the base, melting at 138°, begins to crystallise. If this is not the case, fractional crystallisation from methyl alcohol must be resorted to until separation is complete. The constitutional formulæ of the two bases and their derivatives are discussed fully in the introduction (pp. 722 and 723).

Tetrahydroanhydroisocryptopine,



This base, obtained as described in the last section, separates from methyl alcohol in groups of striated, prismatic needles, and melts at 138—139°:

0·1139 gave 0·2958 CO_2 and 0·0731 H_2O. C=70·8; H=7·1.
0·1253 „ 0·3264 CO_2 „ 0·0804 H_2O. C=71·0; H=7·1.
$C_{21}H_{25}O_4N$ requires C=71·0; H=7·0 per cent.

Tetrahydroanhydroisocryptopine is readily soluble in boiling alcohol, acetone, or benzene, and crystallises well from all these solvents. Discoloured specimens of the base are readily purified by dissolving in dilute hydrochloric acid, digesting with animal charcoal, and precipitating with ammonia. In this condition, the base is soluble in ether, and the ethereal solution, after drying over potassium carbonate and concentrating, deposits the base as a colourless, crystalline crust.

The *salts* with mineral acids are readily soluble, and crystallise from concentrated solutions in needles. Long boiling with concentrated hydrochloric acid does not appear to have any action on the hydrochloride, which separates, on keeping in the ice-chest, in balls of needles. The solution of a crystal of the base in acetic acid gives with sulphuric acid a pale brown coloration, which becomes greenish-brown on keeping, and the addition of a drop of dilute nitric acid changes the colour to deep port wine. The *platinichloride* is obtained, on the addition of platinic chloride to the dilute solution of the hydrochloride, as a pale yellow, caseous precipitate, which soon becomes crystalline. It dissolves appreciably in boiling water, and separates as a heavy, pale orange deposit consisting of groups of irregular plates:

0·1272 gave 0·2069 CO_2 and 0·0507 H_2O. C=44·4; H=4·5.
0·5064 „ 0·0854 Pt. Pt=16·9.
$(C_{21}H_{25}O_4N)_2,H_2PtCl_6$ requires C=45·0; H=4·6; N=17·3 per cent.

The mercurichloride separates, on adding mercuric chloride to the dilute solution of the hydrochloride, as a white, caseous precipitate which soon becomes crystalline; it melts under boiling water, dissolves moderately readily, and, when cooled and rubbed, the milky liquid soon crystallises.

The Methosulphate.—This derivative is readily obtained by adding methyl sulphate (1 c.c.) to the solution of the base (1 gram) in warm benzene, when there is appreciable development of heat, but no immediate separation.* On keeping in the ice-chest, glistening plates soon begin to form, and, after twenty-four hours, the substance is collected and washed with benzene, but it was not recrystallised, because it is very readily soluble both in water and in methyl alcohol.

After drying in the steam-oven, it softened at 145° and melted at about 160°:

0·1185 gave 0·2509 CO_2 and 0·0686 H_2O. C = 57·7; H = 6·4.
$C_{21}H_{25}O_4N,Me_2SO_4$ requires C = 57·4; H = 6·5 per cent.

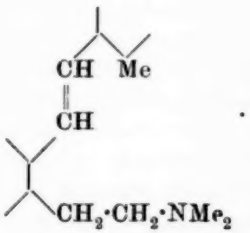
The aqueous solution of this methosulphate gave no precipitate on the addition of ammonia or dilute sodium hydroxide.

The Methiodide.—The addition of hot dilute potassium iodide to the hot aqueous solution of the methosulphate produces a milky liquid, which soon crystallises beautifully in glistening scales:

0·1124 gave 0·2179 CO_2 and 0·0565 H_2O. C = 52·7; H = 5·6.
$C_{21}H_{25}O_4N,MeI$ requires C = 53·1; H = 5·6 per cent.

This methiodide does not become yellow until about 250°, and melts at about 263°, without effervescence, to a lemon-yellow liquid. It is very sparingly soluble in water or alcohol, and separates, when the solution in the latter solvent is concentrated, as a glistening, heavy powder consisting of stout prisms with bevelled edges.

Anhydrotetrahydromethylcryptopine,



This substance is produced when the methosulphate of tetrahydroanhydro*iso*cryptopine is decomposed by methyl-alcoholic potassium hydroxide. The methosulphate (1 gram) was boiled with methyl-alcoholic potassium hydroxide (10 c.c. of 20 per cent.) in an open flask for ten minutes, when decomposition set in readily and a cloudy liquid was produced, which soon deposited a white, crystalline precipitate. The product was mixed with water, heated

* If, however, the benzene solution is boiling, a vigorous reaction sets in, and the methosulphate commences to crystallise at once, the separation being complete in a few minutes.

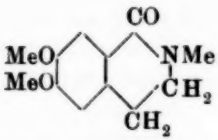
to boiling, the aqueous liquid decanted from the viscid mass, and the latter recrystallised from methyl alcohol, from which it separated in glistening, colourless plates having a striking lilac fluorescence and melting at 107—109°. That this substance was anhydrotetrahydromethylcryptopine was proved by analysis (Found: C = 71·2; H = 7·3; N = 3·9. $C_{22}H_{27}O_4N$ requires C = 71·5; H = 7·3; N = 3·8 per cent.) and by the fact that a mixture of the substance with a specimen of anhydrotetrahydromethylcryptopine which had been prepared from tetrahydromethylcryptopine (899) melted at 106—108°. Moreover, a comparison of the crystals clearly established the identity of the two preparations.

Oxidation of Tetrahydroanhydroisocryptopine.—This oxidation, which has afforded valuable evidence in support of the constitution assigned to the above substance (p. 751), was carried out under the following conditions. The base (9 grams) was dissolved in warm acetone (400 c.c.), the solution cooled to the ordinary temperature, and then very finely powdered and sieved permanganate (13 grams) added in small quantities at a time with vigorous stirring. Oxidation was slow at first, but became more rapid as the temperature rose, and care was taken that the temperature remained below 20° throughout the operation. The product was filtered, the manganese precipitate thoroughly washed with acetone, and the acetone filtrate treated as described below.

When the manganese precipitate was extracted with boiling water, a very slightly coloured filtrate was obtained which, after concentrating considerably, yielded, on acidifying with hydrochloric acid, a very sparingly soluble, nearly colourless, chalky precipitate (2 grams). This was collected and crystallised from glacial acetic acid, from which it separated in needles melting at 215—216°, and yielded on analysis: C = 60·0; H = 4·6, whereas $C_9H_8O_4$ requires C = 60·0; H = 4·5 per cent. Careful comparison showed that this acid was identical with 5:6-methylenedioxy-*o*-toluic acid (916), $CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H$.

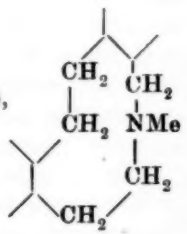
The acetone solution, which had been filtered from the manganese precipitate as described above, was evaporated, when a yellow syrup remained, which gradually deposited needle-shaped crystals. When the whole was distilled in a current of steam, a milky distillate was obtained, which deposited a mass of crystals having the odour of piperonal, and, after recrystallisation from light petroleum, melted at 73—74°. That this substance was 5:6-methylenedioxy-*o*-tolualdehyde, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CHO$, was proved by direct comparison with a specimen of this substance which had previously been obtained by the oxidation of anhydrotetrahydromethylcryptopine (907). The residue in the steam dis-

tillation flask was extracted with ether, the ethereal solution washed with very dilute hydrochloric acid to remove any basic substances, dried over potassium carbonate, and evaporated. When the residual, pale yellow syrup was seeded with a trace of 1-keto-6:7-dimethoxy-2-methyltetrahydro*iso*quinoline,



(m. p. 126°) (Pyman, T., 1909, **95**, 1272; 1910, **97**, 269), it rapidly became crystalline. After remaining in contact with porous porcelain for a couple of days, the colourless, crystalline residue was recrystallised from dry ether, from which it separated in prisms melting at 126°. Moreover, the intimate mixture with a specimen, prepared by the method described by Pyman, melted at the same temperature.

Dihydroanhydrodihydrocryptopine (*A*),



This base, produced by the reduction of *iso*cryptopine chloride under the conditions specified on p. 750, separates from acetone, in which it is rather sparingly soluble, in groups of glistening prisms, and melts at 163—164°:

0·1057 gave 0·2752 CO_2 and 0·0670 H_2O. C = 71·0; H = 7·0.
0·1036 ,, 0·2701 CO_2 ,, 0·0661 H_2O. C = 71·1; H = 7·1.
$C_{21}H_{25}O_4N$ requires C = 71·0; H = 7·0 per cent.

Dihydroanhydrodihydrocryptopine (*A*) is characterised by being remarkably sparingly soluble in boiling methyl alcohol, from which it separates in stars of flat needles; it is much more readily soluble in ethyl alcohol, and readily so in benzene. The solution of a crystal in a drop of acetic acid yields, on mixing with sulphuric acid, at first no coloration, but gradually an intense indigo develops, and the addition of a drop of dilute nitric acid changes this to orange.

The *salts* of dihydroanhydrodihydrocryptopine (*A*) are much less readily soluble in water or dilute acids than those of the isomeric

tetrahydroanhydro*iso*cryptopine (p. 751). When dilute hydrochloric acid is added to the base, the crystals at first dissolve, but almost at once the hydrochloride commences to separate, and is very sparingly soluble in cold dilute hydrochloric acid. It dissolves readily, however, on boiling, and separates in groups of flat needles. The sulphate is also sparingly soluble in dilute sulphuric acid, and crystallises in long hairs radiating from a centre. The base does not dissolve in dilute nitric acid, but is at once converted into the crystalline nitrate, which is more sparingly soluble than either the hydrochloride or sulphate, and separates from its solution in hot dilute nitric acid in stout, prismatic needles with bevelled edges. When boiling dilute solutions of the hydrochloride and potassium iodide are mixed, a clear solution is formed, from which the hydriodide separates in stars of thin laminæ, and is almost insoluble in cold water. The *platinichloride* separates, on the addition of platinic chloride to a hot dilute solution of the hydrochloride, as a viscid, pale ochreous precipitate, which soon hardens; it is somewhat soluble in boiling water and crystallises in microscopic balls of needles:

0·1130 gave 0·1848 CO_2 and 0·0464 H_2O. C = 44·6; H = 4·6.
0·5052 „ 0·0859 Pt. Pt = 17·0.
$(C_{21}H_{25}O_4N)_2,H_2PtCl_6$ requires C = 45·0; H = 4·6; Pt = 17·3 per cent.

The addition of mercuric chloride to the dilute solution of the hydrochloride produces a curdy precipitate resembling silver chloride; this is somewhat soluble in boiling water and separates in stars of prisms.

The picrate is a chrome-yellow precipitate which melts under boiling water and dissolves with difficulty.

The Methosulphate.—When methyl sulphate (1 c.c.) is added to the solution of the base (1 gram) in benzene (10 c.c.), there is no separation at first, but, in a minute or two, the liquid clouds and a viscid syrup is deposited which crystallises on rubbing, the whole becoming a glutinous mass of soft needles. The substance is rather difficult to collect, and is so readily soluble in water or methyl alcohol that it could not be recrystallised. After drying in the steam-oven, it yielded the following analysis:

0·1191 gave 0·2499 CO_2 and 0·0701 H_2O. C = 57·2; H = 6·6.
$C_{21}H_{25}O_4N,Me_2SO_4$ requires C = 57·4; H = 6·5 per cent.

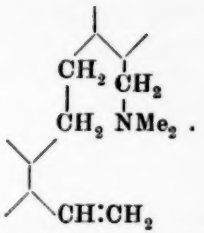
The aqueous solution of this methosulphate gives no precipitate on the addition of ammonia, and a trace of the salt, dissolved in glacial acetic acid, gives no characteristic coloration on the addition of sulphuric acid.

It is mentioned in the introduction (p. 723) that dihydroanhydro-

dihydrocryptopine (*A*) is unusually resistant towards permanganate, and this was evidenced by the following experiment. A few milligrams of very finely powdered permanganate were added to the solution of the base (3 grams) in acetone (150 c.c.), but no appreciable oxidation had taken place after remaining at 0° for fifteen minutes. When the temperature was raised to 20°, oxidation took place more rapidly, and, after 5 grams of permanganate had been reduced, the product, worked up in the usual manner, yielded 0·175 gram of unchanged base. A small quantity of a resinous, sparingly soluble acid was produced, and also an oily base, but the quantities of these were quite insufficient for further investigation.

Reduction of Anhydrodihydrocryptopine (*A*, 938) *to Dihydroanhydrodihydrocryptopine* (*A*).—This conversion, which affords welcome confirmation of the constitution assigned to the last-named substance (p. 723), was carried out under the following conditions: Anhydrodihydrocryptopine (*A*) (m. p. 178°; 7 grams), dissolved in boiling water and concentrated hydrochloric acid (50 c.c.), was poured on freshly prepared 4 per cent. sodium amalgam (350 grams) in an enamelled iron basin, and the whole well stirred until the amalgam had been completely used. The product contained a colourless, satiny mass of needles, and enough boiling water was added to bring the whole into solution. After filtering, excess of ammonia was added, when a caseous mass separated, which was washed with a little cold water and digested with boiling water to dissolve out a quaternary salt which was present (see below). The residue was dissolved in boiling methyl alcohol, when, on keeping, glistening crystals separated which melted at 162—163°, and consisted of dihydroanhydrodihydrocryptopine (*A*), since the admixture with a specimen of this substance which had been prepared by the method described at the commencement of this section melted at 162—164°. The identity was confirmed by analysis. The aqueous ammoniacal filtrate from the base (*A*) deposited, on keeping, a considerable crop of a quaternary salt as a satiny mass of needles. This was collected and identified as *iso*dihydrocryptopine β-chloride (934), since it did not melt at 260°, and, when digested with methyl-alcoholic potassium hydroxide, yielded anhydrodihydrocryptopine (*A*), melting at 178°.

Dihydroisoanhydrodihydromethylcryptopine,

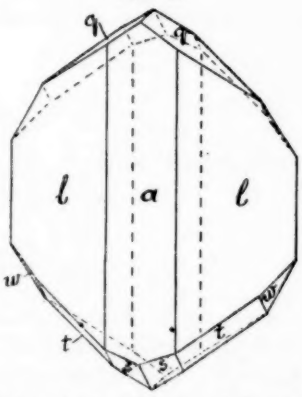


This beautiful substance is obtained when the methosulphate of dihydroanhydrodihydrocryptopine (*A*) is digested with methyl-alcoholic potassium hydroxide. The methosulphate (3 grams) was dissolved in hot methyl alcohol (25 c.c.), mixed with methyl-alcoholic potassium hydroxide (20 c.c. of 20 per cent.), and heated to boiling in an open flask in such a way that there was considerable concentration. The decomposition took place rather slowly, and, after fifteen minutes, the cloudy solution was mixed with water, when a gum separated which showed no signs of crystallisation on rubbing with methyl alcohol. The whole was extracted with pure ether, the ethereal solution carefully washed, dried over potassium carbonate, concentrated, and left in the ice-chest in a corked flask. For some days nothing separated, and then gradually splendid hard, colourless, brilliant prisms began to form, and increased considerably during three weeks:

0·1106 gave 0·2890 CO_2 and 0·0730 H_2O. C = 71·2; H = 7·3.
0·1215 „ 0·3191 CO_2 „ 0·0803 H_2O. C = 71·5; H = 7·4.
$C_{22}H_{27}O_4N$ requires C = 71·5; H = 7·3 per cent.

Dihydroisoanhydrodihydromethylcryptopine melts at 75—77°, and is very readily soluble in the usual solvents. The crystals have been examined by Miss M. W. Porter, with the following results:

FIG. 2.



Dihydroisoanhydrodihydromethylcryptopine.

The substance is monoclinic with axial ratios $a:b:c=0{\cdot}6657:1:0{\cdot}6899$, $\beta=99°34'$. The forms observed are: $a(100)$, $l(210)$, $q(011)$, $s(\bar{2}12)$, $t(\bar{2}32)$, $w(\bar{1}21)$, and, very rarely, $b(010)$, which accordingly is not shown in Fig. 2. Three crystals were measured on the two-circle goniometer, and the mean measured and calculated results are given below:

Face.	No. of readings.	ϕ (Azimuth). Obs.	ϕ (Azimuth). Calc.	ρ (Polar distance). Obs.	ρ (Polar distance). Calc.
a (100)	6	90° 9′	90° 0′	90° 0′	90° 0′
b (010)	1	359 29	0 0	90 0	90 0
l (210)	7	*71 50	—	90 0	90 0
q (011)	3	*13 43	—	*35 23	—
s ($\bar{2}12$)	2	292 0	291 32	42 57	42 13
t ($\bar{2}32$)	6	320 1	319 49	53 10	53 33
w ($\bar{1}21$)	4	329 10	327 39	58 47	58 31

The salts of this base are very readily soluble in water and show little tendency to crystallise. The *platinichloride* was obtained as a pale salmon, chalky precipitate on adding platinic chloride to the dilute solution of the hydrochloride:

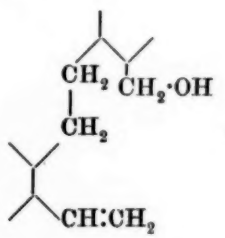
0·1171 gave 0·1981 CO_2 and 0·0518 H_2O. C=46·2; H=4·9.

0·2028 „ 0·0339 Pt. Pt=16·7.

$(C_{22}H_{27}O_4N)_2,H_2PtCl_6$ requires C=46·0; H=4·9; Pt=16·9 per cent.

The solution of a crystal of the base in glacial acetic acid gives, with sulphuric acid, a feeble brown coloration, and the addition of a drop of dilute nitric acid changes this to intense port wine. The methosulphate is obtained by adding methyl sulphate (1 c.c.) to the solution of the base (1 gram) in benzene (5 c.c.), when there is distinct rise of temperature and a syrup separates, which gradually crystallises, especially when triturated with ether. This substance is so readily soluble and so badly characterised that no attempt was made to purify it for the purpose of analysis. Its aqueous solution gives no precipitate on the addition of ammonia.

Dihydro-α-iso*cryptopidol* (947),



This unsatisfactory substance is obtained from the methosulphate of dihydro*iso*anhydrodihydromethylcryptopine by the action of methyl-alcoholic potassium hydroxide, trimethylamine being eliminated.

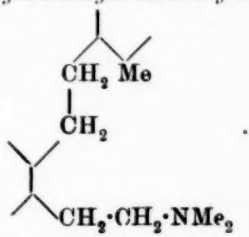
The methosulphate (3 grams), dissolved in a little methyl alcohol, was digested with methyl-alcoholic potassium hydroxide (30 c.c. of 25 per cent.) in an open flask heated just to boiling by means of a salt-solution bath for an hour, the temperature then being raised so that most of the methyl alcohol distilled away and there was no further development of trimethylamine. The residue was mixed with water, the viscid precipitate dissolved in methyl alcohol, mixed with much ether, and the ethereal solution washed with water until quite free from methyl alcohol. After drying over potassium carbonate and concentrating to a small bulk, nothing separated on keeping in the ice-chest for three weeks. The solution was therefore evaporated, when a colourless syrup remained which gradually crystallised, and the buttery mass was left in contact with porous porcelain until dry, but owing to the fact that the substance is so unusually readily soluble in the ordinary solvents and exhibits so little tendency to crystallise, no further purification was possible. After remaining over phosphoric oxide in a vacuum desiccator for a week, the following results were obtained on analysis:

0·1255 gave 0·3201 CO_2 and 0·0798 H_2O. C = 69·6; H = 6·8.

$C_{20}H_{22}O_5$ requires C = 70·2; H = 6·4 per cent.

This result, coupled with its method of formation, clearly indicates that this substance is *dihydro-α-isocryptopidol*.

Section III (c). *Dihydroanhydrotetrahydromethylcryptopine*,



As explained on p. 725, this substance is obtained when the methosulphate either of tetrahydroanhydro*iso*cryptopine (m. p. 138°, p. 752) or dihydroanhydrodihydrocryptopine (*A*) (m. p. 164°, p. 755) is reduced in alkaline solution by sodium amalgam.

(i) *Reduction of the Methosulphate of Tetrahydroanhydro*iso-*cryptopine.*

The solution of this substance (3 grams) in hot water (150 c.c.) is reduced only with considerable difficulty by sodium amalgam (150 grams of 3 per cent.) even on the steam-bath, but a colour-

less oil gradually separates. After the action had proceeded for two hours, the product was left in the ice-chest, when the oil solidified. The mass was well washed and dissolved in hot dilute hydrochloric acid, when, on cooling to 0° and rubbing, the hydrochloride separated as a voluminous mass of needles. This salt, which is very sparingly soluble in dilute hydrochloric acid, but readily so in water, was collected, washed with dilute hydrochloric acid, the cold aqueous solution mixed with ammonia, and the milky liquid extracted with ether. The ethereal solution, dried over potassium carbonate and concentrated, did not yield any crystals on remaining in the ice-chest for a week, but on evaporating off the ether, the residual, colourless syrup suddenly crystallised in balls of needles. After leaving in contact with porous porcelain until traces of oily impurity had been absorbed, the colourless, crystalline residue was dissolved in methyl alcohol, in which it is very readily soluble, and the solution allowed to concentrate nearly to dryness over sulphuric acid in a vacuum desiccator. The mass of plates which separated was drained on porous porcelain and recrystallised from a very small quantity of light petroleum, in which the base is very readily soluble.

(ii) *Reduction of the Methosulphate of Dihydroanhydrodihydrocryptopine* (*A*).

This process was carried out exactly as described under (i), when it was noticed that in the present case the oily base began to separate the moment the hot aqueous solution of the methosulphate was poured on the crushed sodium amalgam. The method of extraction and purification were the same as those described under (i).

The careful examination of the bases obtained from (i) and (ii) showed that both consisted of *dihydroanhydrotetrahydromethylcryptopine*, since both preparations melted at 60—63°, and the mixture also melted at this temperature. The two analyses were made with specimens prepared according to (i) and (ii) respectively:

(i) 0·1126 gave 0·2935 CO_2 and 0·0798 H_2O. C = 71·1; H = 7·9.
(ii) 0·1185 „ 0·3077 CO_2 „ 0·0813 H_2O. C = 70·9; H = 7·9.
$C_{22}H_{29}O_4N$ requires C = 71·1; H = 7·8 per cent.

This base is characterised by its ready solubility in the usual organic solvents; the salts are readily soluble in water, but sparingly so in dilute acids, and generally crystallise well.

The *hydrochloride*, described above, is almost insoluble in cold dilute hydrochloric acid, and melts at 213°. It is very readily

soluble in warm glacial acetic acid, and also in boiling methyl alcohol, and separates from the latter in groups of needles. The addition of potassium iodide to the boiling methyl-alcoholic solution of the hydrochloride gives a clear liquid, from which the hydriodide separates in stars of needles. It is comparatively readily soluble in boiling methyl alcohol, crystallises well, and melts at about 212°. The nitrate separates from dilute nitric acid, in which it is very sparingly soluble, as a felted mass of long hairs. The solution of a crystal of the base in a drop of acetic acid gives scarcely any coloration with concentrated sulphuric acid, but the addition of a drop of dilute nitric acid produces an intense brown, changing to deep cherry-red.

Dihydroanhydrotetrahydromethylcryptopine Methosulphate, $C_{22}H_{29}O_4N,Me_2SO_4$.

This well-characterised derivative separates in needles when the solution of the base (2 grams) in benzene (20 c.c.) is mixed with methyl sulphate (2 c.c.). It was collected, washed with benzene, and dried in the steam-oven, when the glistening crystals became opaque and chalky:

0·1210 gave 0·2577 CO_2 and 0·0747 H_2O. C = 58·0; H = 6·9.
$C_{22}H_{29}O_4N,Me_2SO_4$ requires C = 57·9; H = 7·0 per cent.

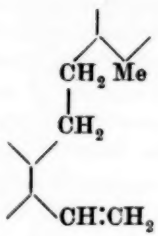
This methosulphate melts at 165—167°, without evolution of gas, to a colourless syrup, and is readily soluble in methyl alcohol or water.

The boiling aqueous solution gives, on the addition of potassium bromide, a milky liquid, from which the methobromide gradually separates in long, well-developed, four-sided, prismatic needles with flat ends.

The *methiodide* is obtained by adding boiling dilute potassium iodide to the boiling dilute aqueous solution of the methosulphate, when the clear solution, on rubbing, deposits tufts of needles:

0·1158 gave 0·2286 CO_2 and 0·0657 H_2O. C = 53·8; H = 6·2.
$C_{22}H_{29}O_4N,MeI$ requires C = 53·8; H = 6·2 per cent.

The dry substance is a satiny mass which darkens at about 230° and melts at about 240° with very little decomposition.

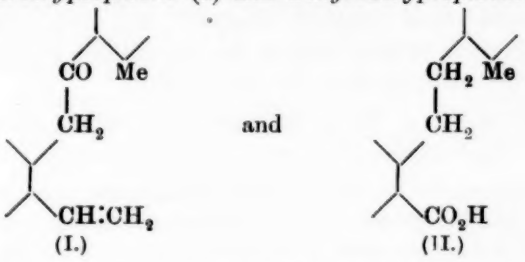
Dihydrocryptopidene, 

This fine substance is obtained when the methosulphate of dihydroanhydrotetrahydromethylcryptopine is decomposed by methyl-alcoholic potassium hydroxide. The methosulphate (1 gram) dissolves readily in warm methyl-alcoholic potassium hydroxide (10 c.c. of 20 per cent.), and trimethylamine is readily eliminated. After boiling for fifteen minutes, the bulk of the methyl alcohol was distilled off, during which the liquid clouded, and, on adding water, a milky liquid was obtained, which was extracted with much ether. The ethereal solution was thoroughly washed, dried over anhydrous potassium carbonate, and rapidly filtered, when the new substance began to separate immediately as a voluminous mass of soft needles, and a further quantity was obtained from the concentrated ethereal solution. For analysis, the substance was recrystallised from ether:

0·1083 gave 0·2932 CO_2 and 0·0673 H_2O. C = 73·8; H = 6·9.
$C_{20}H_{22}O_4$ requires C = 73·6; H = 6·7 per cent.

Dihydrocryptopidene melts at 126—128°, or almost at the same temperature as cryptopidene (m. p. 124°; compare 926), but the mixture of the two substances softens at 105° and is almost completely melted at 108°, so that there can be no question of identity. Moreover, the ethereal solution of dihydrocryptopidene exhibits to only a very slight degree the beautiful lilac fluorescence so characteristic of cryptopidene. Dihydrocryptopidene is unusually sparingly soluble even in boiling methyl alcohol, and separates as a voluminous, woolly mass of needles which fill the entire liquid. The solution of the substance in acetic acid is coloured at first pale brown and then deep cherry-red by sulphuric acid, and a drop of dilute nitric acid changes the colour to intense brown.

Ketodihydrocryptopidene (I) *and Dihydrocryptopidenic Acid* (II),



(I.) (II.)

These interesting substances are produced when dihydrocryptopidene is oxidised in acetone solution with permanganate. The substance (2 grams), dissolved in acetone (150 c.c.), was gradually mixed with finely divided permanganate (3 grams) at the ordinary temperature, when, contrary to expectation, oxidation took place rapidly and with the development of so much heat that cooling was necessary in order to keep the temperature below 15°. The product was filtered, the manganese precipitate (A) washed thoroughly with acetone, and the acetone distilled off, when an almost colourless syrup (0·9 gram) remained, which immediately commenced to crystallise, and crystallisation was much hastened by triturating with methyl alcohol. The product was several times recrystallised from methyl alcohol in order to remove traces of unoxidised dihydrocryptopidene:

0·1151 gave 0·2987 CO_2 and 0·0647 H_2O. C = 70·8; H = 6·2.

$C_{20}H_{20}O_5$ requires C = 70·6; H = 5·9 per cent.

Ketodihydrocryptopidene melts at about 116°, but this melting point is probably not quite accurate, owing to the difficulty of removing the last traces of dihydrocryptopidene. It is characterised by the intense purple coloration which a trace, dissolved in a drop of acetic acid, yields on mixing with much sulphuric acid, and this colour changes to brown on the addition of a drop of dilute nitric acid. When concentrated nitric acid is poured on a trace of the substance rubbed on a watch-glass, a blue solution is produced, and, on warming, a dark green mass separates. Ketodihydrocryptopidene does not yield an acetyl derivative when it is boiled with acetic anhydride and anhydrous sodium acetate, since the unchanged substance separates on the addition of water.

The Semicarbazone.—This derivative was prepared by boiling the alcoholic solution of crude dihydrocryptopidene (as directly obtained from the oxidation of dihydrocryptopidene) with a large excess of a concentrated aqueous solution of semicarbazide acetate for an hour.

On the addition of water, a caseous mass was precipitated, which was separated into the semicarbazone and dihydrocryptopidene by recrystallisation from methyl alcohol. The semicarbazone is sparingly soluble in methyl alcohol, and crystallises as a voluminous mass of needles melting at about 185—190°:

0·1509 gave 13·2 c.c. N_2 at 12° and 766 mm. N = 10·2.

$C_{21}H_{23}O_5N_3$ requires N = 10·6 per cent.

Dihydrocryptopidenic Acid.—The manganese precipitate (*A*, see above) from the oxidation of dihydrocryptopidene was extracted with boiling water, the brown extract boiled with animal charcoal, and acidified, when a viscid acid separated, which gradually hardened and immediately became crystalline on rubbing with glacial acetic acid. This was collected, drained on porous porcelain, and dissolved in boiling glacial acetic acid, from which the new acid separated in long, prismatic needles.

The recrystallised acid yielded the following analytical results:

0·1045 gave 0·2522 CO_2 and 0·0572 H_2O. C = 65·8; H = 6·1.

0·1142 ,, 0·2777 CO_2 ,, 0·0627 H_2O. C = 66·2; H = 6·1.

$C_{19}H_{20}O_6$ requires C = 66·3; H = 5·8 per cent.

Dihydrocryptopidenic acid melts at 194—195°, and is sparingly soluble in cold methyl alcohol, but dissolves more readily on boiling, and crystallises in stars of slender needles; it is almost insoluble in cold water. The solution in glacial acetic acid gives, with sulphuric acid, an olive-brown coloration, which becomes redder on the addition of a drop of dilute nitric acid. When concentrated sulphuric acid is poured on a trace of the acid rubbed on a watch-glass, an intense green colour is produced, which soon changes to purplish-brown, and a green precipitate separates on the addition of water. Concentrated nitric acid does not give a colour reaction with the acid.

The sodium and potassium salts of the acid are readily soluble and give with hydrochloric acid a gelatinous precipitate, which only very gradually becomes crystalline. The titration with *N*/10-sodium hydroxide did not give very accurate results, owing to the uncertainty of the end-point. In one experiment, 0·308 neutralised 0·0385 NaOH, whereas this amount of a monobasic acid, $C_{19}H_{20}O_6$, should neutralise 0·0359 NaOH.

The Anilide, $C_{18}H_{19}O_4{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.—This derivative was prepared mainly with the object of controlling the composition of the acid. The acid was warmed with excess of freshly distilled phosphorus trichloride at 60—70°, when it dissolved completely and with very little discoloration. The excess of the trichloride was then distilled off under reduced pressure and the residue mixed

with much dry ether and excess of aniline. The ethereal solution was washed with very dilute hydrochloric acid, then with water, and the ether evaporated, when a crystalline residue was obtained which was digested with dilute ammonia in order to remove any traces of unchanged acid. Finally, the anilide was recrystallised from glacial acetic acid, from which it separated in glistening needles melting at about 185°:

0·1128 gave 0·2953 CO_2 and 0·0597 H_2O. C = 71·4; H = 5·9.
$C_{25}H_{25}O_5N$ requires C = 71·6; H = 6·0 per cent.

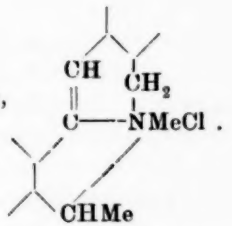
Section IV.

The Quaternary Salts of ψ-Cryptopine.

During the course of this investigation, it has been necessary on several occasions to make a close comparison of certain quaternary salts, thought to be new, with the corresponding quaternary salts of ψ-cryptopine, and this has necessitated a more accurate characterisation of the latter than had been made in Part I. of this research (984).

The following is a brief account of the principal properties of these interesting salts.

ψ-Cryptopine Chloride,



The formation of this salt from anhydrocryptopine methosulphate by boiling with concentrated hydrochloric acid has already been described (984), but the method of preparation there recommended may be simplified in the following manner. Anhydrocryptopine methosulphate (10 grams) is mixed in a small flask with concentrated hydrochloric acid (20 c.c.), gently warmed until solution is complete, and the whole boiled for five minutes in such a way that about a third of the hydrochloric acid escapes; the pale brown syrup is then mixed with two volumes of boiling water. On remaining in the ice-chest, the liquid becomes filled with needles of ψ-cryptopine chloride, which is collected, washed with dilute hydrochloric acid, and recrystallised from this solvent. The yield is about 60 per cent. of that theoretically possible, and a further small quantity may be obtained by allowing the brown mother

liquor to concentrate over solid potassium hydroxide in a vacuum desiccator. The remaining mother liquor contains a considerable quantity of quaternary salt, the nature of which has not been established. When ψ-cryptopine chloride is dried at 100° until it has lost its water of crystallisation, the residue is much discoloured and sometimes brick-red; there was therefore a possibility that the original analysis of the anhydrous chloride was untrustworthy. Further analyses leave, however, no doubt that the chloride has the formula $C_{21}H_{22}O_4NCl$ originally assigned to it, and this is confirmed by the analyses of the iodide, $C_{21}H_{22}O_4NI$, the bromide, $C_{21}H_{22}O_4NBr$, and the platinichloride,

$$(C_{21}H_{22}O_4N)_2PtCl_6.$$

In order to determine the actual composition of the crystallised chloride, two specimens were repeatedly crystallised from dilute hydrochloric acid and left on watch-glasses in the dark until the weight was constant. The substance melted at 117—120° with evolution of steam, solidified again, and then melted at about 150—152°, with evolution of gas, to an orange-red froth. The determination of the water of crystallisation was made by drying in the steam-oven in the case of (*a*) and (*b*), and the analysis (*c*) was done with substance which had been dried over phosphoric oxide in a vacuum desiccator, when the whole of the water was thereby removed with scarcely any discoloration:

(*a*) 0·1389 lost 0·0290. $H_2O = 20·9$.
(*b*) 0·8106 „ 0·1628. $H_2O = 21·1$.
(*c*) 0·1099 gave 0·2611 CO_2 and 0·0593 H_2O. $C = 64·6$; $H = 6·0$.

$C_{21}H_{22}O_4NCl,6H_2O$ contains $H_2O = 21·7$ per cent.
$C_{21}H_{22}O_4NCl$ requires $C = 65·0$; $H = 5·7$ per cent.

Dry ψ-cryptopine chloride crystallises from anhydrous methyl alcohol, in which it is readily soluble, in clusters of needles which, when heated at 100°, become opaque, and the anhydrous residue darkens at 190°, is very dark at 205°, and melts at 210° with effervescence to a black froth:

0·1048 gave 0·2498 CO_2 and 0·0556 H_2O. $C = 65·0$; $H = 5·9$.
$C_{21}H_{22}O_4NCl$ requires $C = 65·0$; $H = 5·7$ per cent.

In addition to the remarkable colour changes already recorded (985), it may be mentioned that the solution of ψ-cryptopine chloride in dilute sulphuric acid gives a reddish-violet on dusting in finely divided manganese dioxide, and an intense cherry-red develops on boiling.

A series of experiments on the action of dilute hydrochloric acid on anhydrocryptopine methosulphate was made with the object of determining whether this substance would behave towards dilute

acids in a manner similar to that which leads, under these conditions, to the formation of the hydroxy*iso*anhydrodihydrocryptopines from anhydrocryptopine itself (994).

The unexpected result was, however, obtained that, even when boiled with dilute hydrochloric acid, anhydrocryptopine methosulphate loses an *N*-methyl group and yields ψ-cryptopine chloride. Thus the methosulphate (2 grams), heated on the steam-bath for forty minutes with concentrated hydrochloric acid (2 c.c.) and water (5 c.c.), gives a deep yellow solution. On keeping in the ice-chest, this deposits a mass of needles which, on examination and analysis, proved to be ψ-cryptopine chloride.

ψ-Cryptopine Bromide, $C_{21}H_{22}O_4NBr$.—In preparing this characteristic salt, carefully purified ψ-cryptopine chloride, dissolved in boiling water, was mixed with a large excess of boiling potassium bromide, when a clear solution resulted, from which microscopic needles soon separated. The bromide was collected, recrystallised from dilute potassium bromide, and then once from water. The air-dry salt contains apparently $5H_2O$, all of which is lost at 95°:

0·1165, heated at 95°, lost 0·0204. $H_2O = 17·6$.

0·1165 gave 0·2476 CO_2 and 0·0533 H_2O. $C = 58·0$; $H = 5·1$.

$C_{21}H_{22}O_4NBr,5H_2O$ contains $H_2O = 17·2$, and $C_{21}H_{22}O_4NBr$ requires $C = 58·3$ and $H = 5·1$ per cent.

This bromide exists in well-defined, dimorphic forms. The needles (*A*) from water, dried at 90°, melt with decomposition at about 130—135°; solidification then takes place, and the next melting point observed is about 230° with effervescence to a reddish-brown froth. When the anhydrous substance (*A*) is boiled with ethyl or methyl alcohol, it dissolves, and the solution now deposits well-developed prisms (*B*), which become opaque in the steam-oven.

The modification (*B*) melts at about 245° with vigorous effervescence to a reddish-brown froth, and crystallises particularly well from glacial acetic acid as a mass of glistening, sulphur-yellow prisms, which Mr. T. V. Barker has described as follows. The macroscopic crystals are strongly doubly refracting, stout, rectangular prisms with straight extinction. In convergent light, an optic axis nearly central. When crystallisation is rapid, there is a marked tendency to form lenticular crystals having diagonal extinction. The modification (*A*) becomes slate-coloured on exposure to light, and is comparatively readily soluble in boiling water, yielding a nearly colourless solution which gelatinises on rapid cooling. Modification (*B*) is sparingly soluble in hot water, and becomes deep salmon on exposure to light. Both modifications

give the remarkable colour reactions which have been described in detail in the case of the corresponding chloride (985).

ψ-Cryptopine Iodide, $C_{21}H_{22}O_4NI$.—This substance has been described (984) as a glistening mass of scales melting at 232—235°.

During the preparation of larger quantities, it was observed that this iodide exists in dimorphic modifications (*A*) and (*B*), melting at 225—227° and 240—242° respectively. When a hot solution of ψ-cryptopine chloride is mixed with hot dilute potassium iodide, a heavy, crystalline precipitate separates, which becomes brick-red at 220°, melts at 232—235°, and consists of modification (*A*). It may be recrystallised from methyl alcohol, if the operation is rapidly carried out, and is obtained in flat, prismatic needles. When, however, it is boiled for a considerable time with methyl alcohol insufficient completely to dissolve it, the needles gradually give place to short, well-defined prisms which are exceedingly sparingly soluble even in boiling methyl alcohol, melt at 240—242°, and consist of modification (*B*). This modification is also sparingly soluble in boiling glacial acetic acid, and separates in iridescent, yellow scales resembling lead iodide, and these, under the microscope, are seen to consist of flat prisms with truncated ends.

ψ-Cryptopine Hydrogen Sulphate, $C_{21}H_{22}O_4N,HSO_4$.—This quaternary salt is obtained when anhydrocryptopine methosulphate (5 grams), dissolved in water (13 c.c.) and sulphuric acid (2 c.c.), is heated for two hours on the steam-bath. On remaining in the ice-chest, the deep yellow solution deposits a crystalline mass which, under the microscope, is seen to consist of warts and to be quite homogeneous.

This was collected, recrystallised from dilute sulphuric acid, in which it is rather sparingly soluble, washed twice with a little water, and drained on porous porcelain. It was then recrystallised from a little water and dried in the steam-oven:

0·1116 gave 0·2315 CO_2 and 0·0530 H_2O. C = 56·5; H = 5·3.

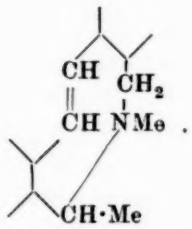
$C_{21}H_{22}O_4N,HSO_4$ requires C = 56·1; H = 5·1 per cent.

ψ-Cryptopine hydrogen sulphate becomes yellow at 180°, deep yellow at 200°, and decomposes at about 215—220° to an orange-red froth.

It exhibits in a very striking manner the characteristic colour reactions described in detail in the case of ψ-cryptopine chloride (985). The relationship of the sulphate to the latter is also evidenced by the fact that, on precipitation with potassium iodide, both yield the (*A*) and (*B*) modifications of ψ-cryptopine iodide (see above). A rather concentrated solution of the sulphate gives, on the addition of dilute nitric acid, an immediate chalky

precipitate of the nitrate; this dissolves on warming and separates in a highly characteristic manner, namely, as an iridescent mass which, under the microscope, is seen to consist of thin, lenticular or boat-shaped plates.

Section IV (a). *The Reduction of ψ-Cryptopine Chloride in Alkaline Solution: Formation of ψ-Anhydrodihydrocryptopine* (*A*) (841),



When ψ-cryptopine chloride (2 grams),* dissolved in water (100 c.c.) and rendered slightly alkaline by the addition of sodium hydroxide, is placed on crushed sodium amalgam (50 grams of 4 per cent.) and the whole heated on the steam-bath, a viscid base soon commences to separate, which gradually crystallises and ultimately becomes quite hard. When the separation was complete, the base was collected, thoroughly washed, dissolved in methyl alcohol, mixed with much ether, and the solution washed until free from methyl alcohol, during which a small quantity of a slimy, quaternary salt separated, which was not examined. After filtering and drying over potassium carbonate, the claret-coloured solution was concentrated considerably and left in the ice-chest, when a thick crust of pale brown prisms gradually separated, which were collected and washed with ether. The mother liquor was evaporated, and the residual purplish-brown syrup mixed with methyl alcohol and nucleated with a crystal from the first crop, when it immediately began to crystallise, and, after collecting and washing with a little methyl alcohol, a considerable pale brown, crystalline mass remained. The combined crops were recrystallised from methyl alcohol, from which the new substance separates splendidly in short, glistening needles growing to stout prisms:

0·1240 gave 0·3255 CO_2 and 0·0728 H_2O. C = 71·5; H = 6·5.

$C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·5 per cent.

* Not more than 2 grams should be employed and the experiment should be conducted as rapidly as possible, otherwise the product will be very dark coloured owing to the formation of a black base due to the action of the alkali on ψ-cryptopine chloride (985).

The prisms have been measured by Mr. T. V. Barker.

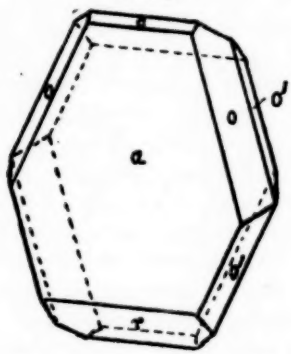
The platy crystals of this substance belong to the monoclinic system. Crystallographic constants: 21°3′, a(73°13′)m(16°47′)b, 43°13′, 74°18′, or, alternatively, $a:b:c=3{\cdot}446:1:2{\cdot}598$, $\beta=105°42'$. The habit of the crystals is shown in Fig. 3, the observed forms being a(100), c(001), $r(\bar{1}01)$, $o'(\bar{1}11)$, and o(111). Two crystals were measured on the two-circle goniometer, with the following results:

	a(100).	c(001).	$r(\bar{1}01)$.	$o'(\bar{1}11)$.	o(111).	
Azimuth	Face of	90° 0′	90° 0′	*21° 3′	21°17′	(21°3′)
Polar distance	reference	*74 18	*116 40	100 18 (100°14′)	69 29	(69 4)

Determinants: $121/1\bar{2}1/10\bar{1}$. Complex-symbol: $3d$; $-1/69\frac{1}{2}/-9\frac{1}{2}$.

Optically, the extinction on a(100) is parallel with the edge ac. In convergent light, a wide biaxial figure is visible through a, indicating the symmetry plane as plane of the optic axes.

FIG. 3.



ψ-Anhydrodihydrocryptopine (*A*) melts at 112°, and is very readily soluble in benzene, ether, or acetone, but sparingly so in light petroleum.

The solution of a trace in a drop of acetic acid gives, with sulphuric acid, a deep orange-red coloration, and the addition of a drop of dilute nitric acid changes this to crimson, which becomes more intense on warming. A trace rubbed on a watch-glass is coloured deep brown by concentrated nitric acid. The hydrochloride and sulphate of the base are readily soluble and exhibit little tendency to crystallise, but the nitrate is characteristic. This salt is obtained, when the base is rubbed with dilute nitric acid, as a crystalline mass very sparingly soluble in cold dilute nitric acid; it dissolves, however, on warming and separates in stars of long, thin plates. The sparing solubility and tendency to crystallise of

this salt have been made use of, with success, in purifying dark-coloured specimens of the crude base. The solution of the sulphate gives, on the addition of potassium iodide, a milky liquid, from which the iodide separates on rubbing, and crystallises from water, in which it is rather readily soluble, in six-sided prisms.

The Methosulphate, $C_{21}H_{23}O_4N,Me_2SO_4$.—The solution of *ψ*-anhydrodihydrocryptopine (*A*) (2 grams) in warm benzene reacts readily with methyl sulphate (2 c.c.) with considerable rise of temperature, and, if a crystal of the methosulphate is introduced and the whole allowed to remain in the ice-chest, a hard crust of nodules separates. If a crystal is not available, the methosulphate generally separates as a syrup, which, however, after washing with ether and stirring with ether, rapidly crystallises. For analysis, the substance was recrystallised from water, in which it is readily soluble; it separates in groups of short, prismatic needles:

0·1177 gave 0·2460 CO_2 and 0·0646 H_2O. C = 57·1; H = 6·1.
$C_{21}H_{23}O_4N,Me_2SO_4$ requires C = 57·6; H = 6·1 per cent.

ψ-Anhydrodihydrocryptopine (A) *methosulphate* melts at 175—180° with some effervescence, but without darkening; the solution of a trace in acetic acid gives with sulphuric acid a deep burnt sienna coloration, becoming intense permanganate on the addition of a drop of dilute nitric acid. It is readily soluble in hot methyl alcohol, and when boiled with methyl-alcoholic potassium hydroxide, the solution becomes deep violet, especially where it comes in contact with the air; the colour then changes to bluish-violet, then to sage-green; the addition of hydrochloric acid destroys the green colour and yields a clear, burnt sienna solution.

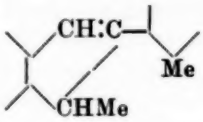
The Methiodide, $C_{21}H_{23}O_4N,MeI$.—The addition of hot dilute potassium iodide to the hot dilute solution of the methosulphate results in a clear solution, from which the methiodide immediately begins to separate in well-developed, six-sided prisms with bevelled edges:

0·1172 gave 0·2315 CO_2 and 0·0602 H_2O. C = 53·9; H = 5·7.
$C_{21}H_{23}O_4N,MeI$ requires C = 53·3; H = 5·3 per cent.

ψ-Anhydrodihydrocryptopine methiodide is sparingly soluble in boiling methyl alcohol, and separates in long, prismatic needles radiating from a centre. It melts at 197—200°, with vigorous effervescence to a yellow froth.

Oxidation of ψ-Anhydrodihydrocryptopine (*A*).—When this base (2 grams) was treated in acetone solution with powdered permanganate (2·5 grams), it was noticed that oxidation was slow, and, on working up the product, about half the substance was

recovered unchanged. The aqueous extract from the manganese precipitate yielded, on concentrating and acidifying, a small quantity of a highly coloured acid resembling amorphous phosphorus, and this did not appear to contain any 5:6-methylenedioxy-*o*-toluic acid (compare p. 728).

ψ-Cryptopidene, 

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This characteristic substance is produced directly from ψ-anhydrodihydrocryptopine (*A*) methosulphate by reduction with sodium amalgam in faintly alkaline solution. The methosulphate (8 grams), dissolved in hot water (200 c.c.), was poured on crushed sodium amalgam (150 grams of 3 per cent.) in a flat basin, when, on heating on the steam-bath, there was an immediate odour of dimethylamine, and a crystalline scum began to rise to the surface. After about half an hour, there was no further separation; the whole was therefore filtered, and the colourless, crystalline residue washed and recrystallised from methyl alcohol. The yield appeared to be almost that theoretically possible:

0·1121 gave 0·3052 CO_2 and 0·0628 H_2O. C = 74·2; H = 6·2.
$C_{20}H_{20}O_4$ requires C = 74·1; H = 6·2 per cent.

ψ-Cryptopidene melts at 142—144°, and cannot be identical with *iso*-ψ-cryptopidene (m. p. 152°, p. 776), since the mixture of the two substances melts at about 130—132° with previous softening. It is sparingly soluble in cold methyl alcohol, but dissolves more readily on boiling, and separates in groups of nearly colourless, glistening needles. It dissolves readily in boiling alcohol, benzene, acetone, or acetic acid, but is sparingly soluble in ether or light petroleum. It crystallises well from light petroleum in six-sided plates, and from acetone or dilute acetic acid in needles. The solution of a trace in acetic acid gives, with sulphuric acid, a burnt sienna coloration which, on the addition of a drop of dilute nitric acid, becomes deep brown. Concentrated nitric acid dissolves the substance to a deep brown solution, which gradually fades. A crystal of the substance dissolved in acetic acid gives, with manganese dioxide and dilute sulphuric acid, an intense brown solution.

ψ-Cryptopidene does not appear to be reduced when its solution in boiling alcohol is treated with sodium (compare p. 745).

Oxidation of ψ-Cryptopidene.—In this experiment, the substance (3·5 grams), dissolved in acetone (200 c.c.), was oxidised by the gradual addition of finely powdered permanganate (5 grams) at

the ordinary temperature. The product was filtered, and the manganese precipitate, after thoroughly washing with acetone, extracted with boiling water. The brown, alkaline extract was nearly neutralised, boiled with animal charcoal, concentrated, and acidified, when an acid (0·5 gram) separated which crystallised from acetic acid in needles, melted at 214—216°, and was recognised as 5:6-methylenedioxy-*o*-toluic acid (916). The acetone extract from the oxidation yielded, on evaporation, a syrupy mass (2·9 grams), which, when rubbed with methyl alcohol, immediately crystallised. After filtering and leaving in contact with porous porcelain, the yellow mass was once crystallised from methyl alcohol, when it separated in pale yellow needles melting at about 128°. On careful fractional crystallisation from methyl alcohol, three distinct kinds of crystals were observed; these were mechanically separated, and each kind was recrystallised. The three constituents were found to be (i) unchanged ψ-cryptopidene melting at 140—142°; *dioxy-ψ-cryptopidene*, $C_{20}H_{18}O_6$, melting at 138—140° and crystallising in light, woolly balls; *trioxy-ψ-cryptopidene*, $C_{20}H_{18}O_7$, melting at 165° and crystallising in hard, single, sulphur-yellow prismatic needles.

The analysis of *dioxy-ψ-cryptopidene* yielded the following results:

0·1071 gave 0·2640 CO_2 and 0·0481 H_2O. C = 67·2; H = 5·2.
$C_{20}H_{18}O_6$ requires C = 67·8; H = 5·1 per cent.

The solution of a trace of this substance in acetic acid gives with sulphuric acid an intense brown coloration, becoming purplish-brown and then cherry-red on the addition of a drop of dilute nitric acid. It reacts readily when its solution in methyl alcohol is boiled with excess of semicarbazide hydrochloride and sodium acetate, and a crystalline precipitate of the *semicarbazone* separates which is very sparingly soluble in methyl alcohol.

Found: N = 11·3.
$C_{21}H_{21}O_6N_3$ requires N = 10·2 per cent.

The behaviour of dioxy-ψ-cryptopidene towards alkalis resembles that of benzoin or benzil. Methyl-alcoholic potassium hydroxide does not immediately colour the substance, but gradually a reddish-brown develops, and, on warming, this becomes intense reddish-brown, then pink, and then gradually fades.

The product, diluted with water, yields a pale brown solution, and hydrochloric acid precipitates an amorphous acid which, on warming, becomes crystalline.

Trioxy-ψ-cryptopidene (m. p. 165°) yielded the following analytical results:

0·1070 gave 0·2539 CO_2 and 0·0478 H_2O. C = 64·7; H = 5·0.
$C_{20}H_{18}O_7$ requires C = 64·9; H = 4·9 per cent.

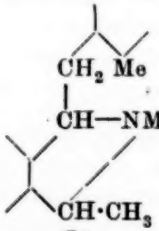
The acetic acid solution of a trace of this substance is coloured yellowish-brown by sulphuric acid, and the addition of a drop of dilute nitric acid changes this first to port-wine colour and then to intense burnt sienna. It also reacts very readily when its solution in boiling methyl alcohol is mixed with excess of a saturated aqueous solution of semicarbazide hydrochloride and sodium acetate, and a voluminous, rather gelatinous precipitates separates which appears to be the *disemicarbazone* mixed probably with some of the mono-derivative.

Found: N = 15·7.
$C_{21}H_{21}O_7N_3$ requires N = 9·8; $C_{22}H_{24}O_7N_6$ requires N = 17·3 per cent.

Trioxy-ψ-cryptopidene, like the corresponding dioxy-derivative (see above), exhibits the benzil reaction in a striking manner. The powdered substance is rapidly coloured brown when mixed with methyl-alcoholic potassium hydroxide, and dissolves to an intense reddish-brown solution, which becomes pink in contact with air, and then soon fades, but not completely. The solution of the product in water is pale salmon, and yields a brick-red, crystalline precipitate on the addition of dilute hydrochloric acid.

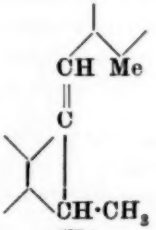
Constitutional formulæ which appear to be in harmony with the properties of dioxy- and trioxy-ψ-cryptopidene are suggested on p. 729.

Section IV (b). *The Reduction of ψ-Cryptopine Chloride in Acid Solution: Formation of Dihydroanhydro-ψ-cryptopine* (I) *and* iso-ψ-*Cryptopidene* (II),



(I.)

and



(II.)

In studying this curious reduction, ψ-cryptopine chloride (5 grams), dissolved in water (80 c.c.) and concentrated hydrochloric acid (15 c.c.), was treated at the boiling temperature, in an enamelled iron basin, with sodium amalgam (200 grams of 4 per cent.), which was added all at once. The whole was well

stirred during the reduction, and care was taken, by frequently adding small quantities of hydrochloric acid, that the liquid was always strongly acid. During the process, a white, crystalline, insoluble substance (iso-*ψ-cryptopidene*) separated in quantity equal to about 8 per cent. of the *ψ*-cryptopine chloride employed; this was collected, and its examination is described on p. 776.

The acid filtrate from this neutral substance was mixed with excess of ammonia, when a caseous precipitate separated which, on shaking, became chalky, and this was collected, washed, and drained on porous porcelain. The nearly colourless mass was dissolved in methyl alcohol and poured into a large volume of ether, when a flocculent precipitate of unchanged *ψ*-cryptopine chloride separated, which was collected and well washed with ether. The pale brown ethereal filtrate was washed with water until free from methyl alcohol, dried over potassium carbonate, and concentrated to a small bulk, but nothing separated after remaining in the ice-chest for a week. When the ether was evaporated, a syrup remained which, over phosphoric oxide in a vacuum desiccator, became a friable mass like colophony, and consisted of almost pure *dihydroanhydro-ψ-cryptopine*:

0·1265 gave 0·3271 CO_2 and 0·0806 H_2O. C = 70·5; H = 7·0.

$C_{21}H_{25}O_4N$ requires C = 71·0; H = 7·0 per cent.

All attempts to obtain this base in a crystalline condition were unsuccessful, and it is fortunate that it yields a characteristic *picrate* which separates as a deep ochreous, amorphous precipitate when picric acid is added to the aqueous solution of the hydrochloride. This double salt melts under boiling water, and is sparingly soluble in boiling methyl alcohol, from which it separates in deep orange leaflets. After drying in the steam-oven, the substance becomes yellow at 110°, shrinks at 180°, and melts at about 195—197° to a reddish-brown syrup:

0·1021 gave 8·7 c.c. N_2 at 13° and 755 mm. N = 10·0.

$C_{21}H_{25}O_4N,C_6H_3O_7N_3$ requires N = 9·6 per cent.

This picrate was decomposed by ammonia, the base extracted with ether, the ethereal solution washed, dried over potassium carbonate, evaporated, and the syrup left over phosphoric oxide in a vacuum desiccator until it became a friable resin and the weight was constant. The analysis then yielded C = 70·9; H = 7·0, agreeing well with the formula $C_{21}H_{25}O_4N$, which requires C = 71·0; H = 7·0 per cent.

Oxidation of Dihydroanhydro-ψ-cryptopine.—When the solution of the base (1 gram) in acetone is treated with finely divided permanganate (1·2 grams), oxidation takes place moderately readily at 15°.

The manganese precipitate, after thoroughly washing with acetone, yielded on extraction with hot water a deep brown solution, from which hydrochloric acid precipitated a dark, resinous acid. This was collected, boiled with much water, the extract decolorised with animal charcoal, neutralised with sodium carbonate, and evaporated to a small bulk.

On acidifying the nearly colourless solution, a chalky acid separated, which crystallised from acetic acid as a colourless, satiny mass, melted at 214—216°, and was recognised as 5 : 6-methylenedioxy-*o*-toluic acid, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H$ (916). The acetone solution from the oxidation deposited a syrup on evaporation which was only partly soluble in warm dilute hydrochloric acid, but the amount was too small for further investigation.

iso-*ψ*-*Cryptopidene*, $C_{20}H_{20}O_4$.—The neutral substance formed during the reduction of *ψ*-cryptopine chloride (see above) was well washed, dried on porous porcelain, and twice recrystallised from methyl alcohol:

0·1047 gave 0·2838 CO_2 and 0·0598 H_2O. C = 73·9; H = 6·3.
0·1023 „ 0·2768 CO_2 „ 0·0553 H_2O. C = 73·8; H = 6·0.
$C_{20}H_{20}O_4$ requires C = 74·1; H = 6·0 per cent.

iso-*ψ*-*Cryptopidene* melts at 150—152°, and is moderately soluble in boiling methyl alcohol, from which it crystallises in glistening plates resembling benzoic acid. It dissolves readily in benzene, but is almost insoluble in light petroleum, and separates, when the hot solution in benzene is mixed with light petroleum, in thin, rhombic plates.

It also crystallises well from acetone in almost square plates with bevelled edges. It is readily soluble in boiling glacial acetic acid, much less so in the cold, and separates splendidly as a satiny mass of thin, rectangular plates. The solution of a crystal in a drop of acetic acid gives, on the addition of sulphuric acid, a deep brown coloration, which becomes much more intense on adding a drop of dilute nitric acid.

A trace of the substance rubbed on a watch-glass dissolves in concentrated nitric acid, and the intense indigo-blue coloration produced soon changes to brown. The most characteristic reaction of the substance is the intense pink colour, changing to brown, which develops when finely powdered manganese dioxide and a little dilute sulphuric acid is added to the solution in dilute acetic acid. *iso-ψ*-Cryptopidene does not appear to be readily reduced when its solution in boiling alcohol is treated with sodium.

Oxidation of iso-*ψ*-*Cryptopidene to Ketodihydro*iso-*ψ*-*cryptopidene.*—*iso-ψ*-Cryptopidene is scarcely attacked when its solution in acetone is mixed with permanganate at −10°, and action is

very slow even at the ordinary temperature. In order to study this oxidation, the substance (1·4 grams), dissolved in acetone (50 c.c.), was, during two days, gradually mixed with very finely powdered and sieved permanganate (2 grams).

The product was filtered, the manganese precipitate thoroughly washed with acetone (*B*), and extracted with boiling water. The brown, aqueous solution was decolorised with animal charcoal, concentrated, and acidified, when a small quantity of a solid acid separated which crystallised from acetic acid in satiny plates, melted at 215—217°, and consisted of 5:6-methylenedioxy-*o*-toluic acid (916).

The acetone solution (*B*) deposited, on evaporation, a yellow syrup, and this yielded, when distilled in a current of steam, a small quantity of 5:6-methylenedioxy-*o*-tolualdehyde (907), which separated from the distillate in needles and melted at 72—74°. The residue in the steam distillation flask was extracted with ether, the ethereal solution thoroughly dried over potassium carbonate, and evaporated, when a syrup remained, which soon crystallised. After remaining in contact with porous porcelain until oily impurity had been removed, the almost colourless residue was fractionally crystallised from methyl alcohol, and thus separated into unchanged *iso*-ψ-cryptopidene and a new substance, which crystallised in glistening plates, melted at about 135°, and consisted of *ketodihydro*iso-ψ-*cryptopidene*. Unfortunately, the small amount of material available did not allow of the removal of the last traces of *iso*-ψ-cryptopidene, so that the melting point must be taken as approximate only:

0·1102 gave 0·2861 CO_2 and 0·0589 H_2O. C=70·8; H=5·9.

$C_{20}H_{20}O_5$ requires C=70·6; H=5·9 per cent.

The small remainder of the substance was dissolved in boiling methyl alcohol, digested with excess of semicarbazide hydrochloride and sodium acetate for two hours, and evaporated to dryness. The nearly white residue was washed with water and crystallised from alcohol, from which it separated in needles:

0·1001 gave 0·2348 CO_2 and 0·0522 H_2O. C=64·0; H=5·9.

$C_{21}H_{23}O_5N_3$ requires C=63·5; H=5·8 per cent.

Attempts to hydrolyse this *semicarbazone* with a view to obtaining the pure keto-derivative were unsuccessful, since boiling with concentrated hydrochloric acid converts it into a substance which crystallises from methyl alcohol in needles, melts at about 225°, and is possibly an indole derivative. A constitutional formula for ketodihydro*iso*-ψ-cryptopidene is suggested on p. 730.

Section IV (c). *The Reduction of ψ-Methylberberinium Chloride: Formation of* iso-*ψ-Berberidene and Dihydroanhydro-ψ-methylberberine.*

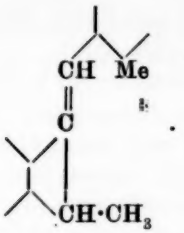
This reduction was carried out essentially under the conditions described in detail in the case of the acid reduction of ψ-cryptopine chloride (p. 774), 300 grams of 4 per cent. amalgam being employed for the reduction of 8 grams of the chloride. During the process, a scum separated, which at first was crystalline, but later melted to a brown syrup, and, after the product had cooled, this was extracted with ether (*A*), the ethereal solution well washed, dried over potassium carbonate, and evaporated, when a syrup remained which showed no signs of crystallising. However, on rubbing with methyl alcohol, crystallisation soon commenced, and, after collecting and washing with methyl alcohol, the pale salmon mass was twice recrystallised from this solvent:

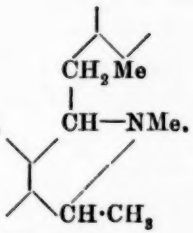
0·1187 gave 0·3207 CO_2 and 0·0677 H_2O. C = 73·7; H = 6·3.
0·1195 „ 0·3245 CO_2 „ 0·0687 H_2O. C = 74·1; H = 6·4.
$C_{20}H_{20}O_4$ requires C = 74·1; H = 6·2 per cent.

iso-*ψ-Berberidene* melts at 117° and is sparingly soluble in methyl alcohol, yielding a lilac, fluorescent solution, from which it separates in well-developed prismatic needles. It is very readily soluble in benzene, but less so in light petroleum, and separates from the mixture of these solvents particularly well in brilliant, elongated prisms. It also crystallises well from light petroleum alone or from ether, in which it is readily soluble, or from acetic acid, in glistening prisms.

A trace of the substance rubbed on the side of a test-tube is coloured deep violet, changing to brown by concentrated nitric acid.

The solution in acetic acid is coloured yellowish-brown on the addition of sulphuric acid, and a drop of dilute nitric acid changes the colour to an intense reddish-brown. When manganese dioxide and a little dilute sulphuric acid are added to the solution in acetic acid in the cold, a pink colour gradually develops, and, on warming, this changes to brown and then to yellow. The relationship of *iso-ψ*-berberidene and *iso-ψ*-cryptopidene is discussed on p. 731, and it may be pointed out that the striking similarity in their properties is doubtless due to their both containing the characteristic grouping





Dihydroanhydro-ψ-methylberberine,

The acid liquors (*A*) from the reduction of ψ-methylberberinium chloride, which had been extracted with ether, as already described, were made strongly alkaline with ammonia, and the turbid liquid thoroughly extracted with ether. On evaporation, the ethereal solution deposited a syrup, which was only partly soluble in dilute hydrochloric acid.

The whole was warmed with very dilute hydrochloric acid, filtered, and the filtrate precipitated with excess of picric acid, when a voluminous, viscid mass separated, which soon hardened. This was collected, left on porous porcelain until dry, and recrystallised from methyl alcohol, from which it separated in orange-red balls, and melted at 115—120° to an orange-red syrup:

0·1108 gave 0·2286 CO_2 and 0·0469 H_2O. C = 56·1; H = 4·7.

0·1027 „ 8·6 c.c. N_2 at 14° and 756 mm. N = 9·8.

$C_{21}H_{25}O_4N,C_6H_3O_7N_3$ requires C = 55·5; H = 4·7; N = 9·6 per cent.

This *picrate* was decomposed by warming with dilute ammonia, the base extracted with ether, the ethereal solution thoroughly washed, dried over potassium carbonate, and evaporated, when a syrup remained which, over phosphoric oxide in a vacuum desiccator, dried to a friable resin:

0·1271 gave 0·3292 CO_2 and 0·0817 H_2O. C = 70·6; H = 7·1.

$C_{21}H_{25}O_4N$ requires C = 71·0; H = 7·0 per cent.

Dihydroanhydro-ψ-methylberberine exhibits little tendency to crystallise, but it seems to become crystalline when left in a closed tube in contact with a little methyl alcohol. The hydrochloride is very readily soluble and gives, on the addition of platinic chloride, an ochreous, caseous precipitate of the *platinichloride* which, on warming, becomes chalky:

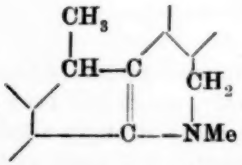
0·1217 gave 0·2040 CO_2 and 0·0521 H_2O. C=45·7; H=4·7.
0·2054 ,, 0·0351 Pt. Pt=17·1.
$(C_{21}H_{25}O_4N)_2,H_2PtCl_6$ requires C=45·1; H=4·7; Pt=17·3 per cent.

The addition of boiling dilute aqueous potassium iodide to the boiling dilute solution of the hydrochloride gave a milky liquid, from which a yellow syrup separated. This dissolved readily in methyl alcohol, and the solution, on spontaneous evaporation, deposited a crystalline mass of the *hydriodide*, which was drained on porous porcelain, dried in the steam-oven, and analysed:

0·1117 gave 0·2141 CO_2 and 0·0539 H_2O. C=52·2; H=5·3.
$C_{21}H_{25}O_4N,HI$ requires C=52·2; H=5·4 per cent.

Section V.

Derivatives of iso*Anhydrocryptopine,*



The *iso*anhydrocryptopine required for these experiments was prepared by the method already given (1002), and certain direct derivatives of this substance, not previously described, were obtained during the course of the investigation.

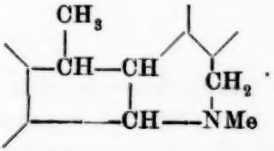
iso*Anhydrocryptopine Methochloride*, $C_{21}H_{21}O_4N,MeCl$.—This characteristic derivative is readily obtained when *iso*anhydrocryptopine methiodide (1005), ground to a paste with much water, is digested on the steam-bath with excess of silver chloride for an hour. The filtrate, on concentration, deposits the methochloride as a hard crust of pale lemon-yellow prisms; after remaining exposed to the air until the weight was constant, this quaternary salt contained two molecules of water, and became opaque on drying at 100°:

1·7754 lost 0·1493 at 100°. H_2O=8·4.
$C_{21}H_{21}O_4N,MeCl,2H_2O$ contains H_2O=8·2 per cent.
0·1075 (dried at 100°) gave 0·2577 CO_2 and 0·0575 H_2O. C=65·4; H=5·9.
$C_{21}H_{21}O_4N,MeCl$ requires C=65·7; H=6·0 per cent.

iso*Anhydrocryptopine methochloride* melts at about 233° with vigorous decomposition to a black froth. It is very readily soluble in hot, but much less so in cold, water, and the addition of hydrochloric acid does not appear greatly to reduce the solubility. The aqueous solution gives no precipitate with ammonia or dilute sodium hydroxide.

The anhydrous salt dissolves readily in boiling methyl alcohol and separates, on cooling, in long, flat prisms which are quite colourless.

When the cold aqueous solution is mixed with dilute sulphuric acid and then a little manganese dioxide dusted in, a pale blue coloration gradually develops, which deepens on warming. The addition of dilute permanganate at 0° to the aqueous solution produces at first a purple precipitate of the permanganate, and then oxidation rapidly takes place.

Dihydroisoanhydrocryptopine, 

This base was obtained by the reduction of *iso*anhydrocryptopine under the following conditions. The hydrochloride of *iso*anhydrocryptopine* (1004) (3 grams), dissolved in dilute acetic acid and sodium acetate, was gradually treated with crushed sodium amalgam (200 grams of 3 per cent.) at about 80°. When the amalgam was exhausted, the filtered solution was mixed with ammonia, the chalky precipitate collected, and dissolved in hot dilute hydrochloric acid. On long keeping in the ice-chest, the very sparingly soluble *hydrochloride* of *dihydroisoanhydrocryptopine* separated, and was collected and recrystallised from dilute hydrochloric acid,† from which it separates in groups of colourless prisms; it darkens at 210° and decomposes at about 215—218° with vigorous effervescence to an orange-red froth:

0·1101 gave 0·2619 CO_2 and 0·0625 H_2O. C = 64·5; H = 6·3.

$C_{21}H_{23}O_4N$,HCl requires C = 64·7; H = 6·2 per cent.

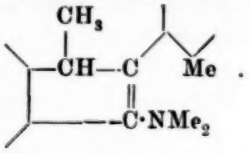
This hydrochloride is comparatively readily soluble in hot water, but very sparingly so in dilute hydrochloric acid. The base, obtained by adding ammonia to the dilute aqueous solution of the hydrochloride, is a gelatinous precipitate becoming granular on warming, but all attempts to recrystallise the substance were unsuccessful. The precipitate, thoroughly washed, was dried over phosphoric oxide in a vacuum desiccator:

* This hydrochloride, like that of anhydrocryptopine (977), is dissociated when sodium acetate is added to its aqueous solution.

† The mother liquors of this hydrochloride contain the hydrochloride of a second base which also has the composition $C_{21}H_{23}O_4N$, and it is probable that the two bases represent stereoisomeric modifications of the same substance.

0·1070 gave 0·2801 CO_2 and 0·0621 H_2O. C = 71·2; H = 6·4.
$C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·5 per cent.

Section V (a). *The Reduction of* iso*Anhydrocryptopine Methosulphate in Alkaline Solution* (p. 732): *Formation of Dihydromethyl*iso*anhydrocryptopine*, (*A*) *and* (*B*),



The *iso*anhydrocryptopine methosulphate used in these experiments was prepared by adding methyl sulphate to the benzene solution of *iso*anhydrocryptopine in the manner already described (1005). The carefully purified substance (5 grams), dissolved in boiling water (300 c.c.), was vigorously stirred with crushed sodium amalgam (150 grams of 3 per cent.), when a base separated, sometimes in crystalline form, but more frequently as a gum, which ultimately crystallised. The whole was heated on the steam-bath until no further separation could be observed; the base was then collected, washed well, dried on porous porcelain, and dissolved in boiling methyl alcohol. When this solution is allowed to remain without agitation, the modification (*A*) of *dihydromethyl*iso*anhydrocryptopine* separates as a bulky mass of soft needles, but gradually pale yellow prisms of the modification (*B*) make their appearance, and, if the hot solution is stirred during crystallisation, the separation consists entirely of this modification. The prisms (*B*) melt sharply at 121—122°, but, when the needles (*A*) are slowly heated in a capillary tube, it is noticed that they sinter at about 105°, clearly owing to transition into the prismatic modification, and the melting point is again 121—122°. Both modifications were analysed:

(*A*) 0·1098 gave 0·2908 CO_2 and 0·0687 H_2O. C = 72·2; H = 7·0.

(*B*) 0·1101 gave 0·2906 CO_2 and 0·0685 H_2O. C = 72·0; H = 6·9.

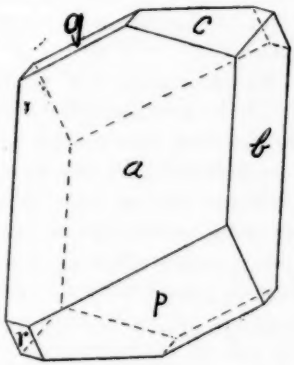
$C_{22}H_{25}O_4N$ requires C = 71·0; H = 6·8 per cent.

Crystals of this substance were kindly examined by Miss M. W. Porter, who reports that the system is anorthic, with $a:b:c = 0·728:1:0·766$, $\alpha = 100°15'$, $\beta = 104°23'$, $\gamma = 95°2'$. The following forms were observed: $b(010)$, $a(100)$, $c(001)$, $q(0\bar{1}1)$, $r(\bar{1}01)$, and $p(\bar{1}\bar{1}1)$. The habit, as is shown in Fig. 4, is prismatic, and the

vertical faces are generally curved. Following are the mean measurements derived from three crystals:

	Azimuth.	Polar distance.
b (010)	0° 0′	90° 0′
a (100)	*82 2	90 0
c (001)	*49 33	*18 37
q (0$\bar{1}$1)	155 8	32 25
r ($\bar{1}$01)	275 24	39 25
q ($\bar{1}\bar{1}$1)	*229 4	*47 42

FIG. 4.



Dihydromethylisoanhydrocryptopine (B), m. p. 122°.

The solution of a trace of either modification in a drop of acetic acid gives with sulphuric acid a deep orange-red coloration, which becomes intense port wine and then brown on the addition of dilute nitric acid. *Dihydromethylisoanhydrocryptopine* is very readily soluble in cold dilute hydrochloric acid, but, on rubbing, the sparingly soluble crystalline hydrochloride immediately separates. This fine salt is readily soluble in hot water, and crystallises in short, six-sided prisms with obliquely cut-off ends. The sulphate does not crystallise under these conditions, but the addition of dilute nitric acid to the solution of the sulphate causes the nitrate to separate as a syrup, which crystallises on rubbing.

The Methosulphate.—This characteristic derivative is readily prepared by adding methyl sulphate (3 c.c.) to the solution of the base (2·5 grams) in a little warm benzene, when combination takes place immediately with the evolution of much heat. The liquid soon becomes a pasty mass of crystals, and these are collected, washed with benzene, and recrystallised from water or methyl alcohol:

0·1094 gave 0·2334 CO_2 and 0·0623 H_2O. C = 58·2; H = 6·3.
$C_{22}H_{25}O_4N,Me_2SO_4$ requires C = 58·4; H = 6·3 per cent.

Dihydromethylisoanhydrocryptopine methosulphate melts at about 202°, without effervescence, to a colourless syrup, and is readily soluble in hot water, from which it separates in groups of flat needles; the aqueous solution gives no precipitate on the addition of ammonia. It dissolves very readily in boiling methyl alcohol, but is much less soluble in the cold and separates in thin plates with obliquely cut-off ends. When warmed with methyl-alcoholic potassium hydroxide (15 per cent.), it dissolves, and, on boiling, decomposition slowly sets in with the elimination of trimethylamine; the liquid becomes brown, then deep purple, and finally nearly black, and the addition of water then precipitates a black substance (compare 985).

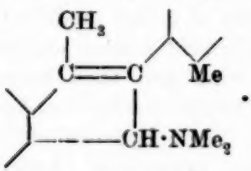
The Methiodide.—The addition of hot dilute potassium iodide to the hot dilute solution of the methosulphate produces no immediate precipitate, but the liquid soon clouds, and a gum separates which, on rubbing, readily crystallises. If this gum is dissolved in boiling alcohol and the solution stirred, the methiodide separates as a sandy precipitate consisting of curious, circular warts:

0·1121 gave 0·2215 CO_2 and 0·0563 H_2O. C = 53·9; H = 5·6.

$C_{22}H_{25}O_4N$,MeI requires C = 54·2; H = 5·5 per cent.

This *methiodide* melts at about 215—217° to a yellow syrup.

ψ-Dihydromethylisoanhydrocryptopine (p. 732),



This substance is obtained (*a*) from *iso*anhydrocryptopine methochloride (p. 780) by reduction in hydrochloric acid solution with sodium amalgam, or (*b*) from dihydromethyl*iso*anhydrocryptopine by boiling with dilute hydrochloric acid. (*a*) *iso*Anhydrocryptopine methochloride (3 grams), dissolved in hot water (200 c.c.) and hydrochloric acid (30 c.c.), is treated with sodium amalgam (120 grams of 4 per cent.) on the steam-bath. When reduction is complete, the liquid is filtered from a trace of a chalky, neutral substance, the filtrate mixed with ammonia, the rather gelatinous precipitate collected, washed, dried on porous porcelain, and dissolved in a little boiling methyl alcohol, in which it is very readily soluble. If the solution is cooled in ice and salt and rubbed, crystallisation gradually sets in, and, on recrystallisation, pure *ψ-dihydromethylisoanhydrocryptopine* is obtained in colourless needles melting at

140—141°. (*b*) Dihydromethyl*iso*anhydrocryptopine (1 gram), dissolved in concentrated hydrochloric acid (2 c.c.) and water (10 c.c.), is boiled for ten minutes in an open test-tube by means of a sulphuric-acid bath in such a way that concentration to about half the volume takes place. At first there is no visible change, but towards the end of the operation a pale green develops. The cold product yields a caseous precipitate on the addition of ammonia, which soon becomes hard, and the substance separates from methyl alcohol in microscopic groups of needles melting at 140—141°. Analyses were made with substances prepared by methods (*a*) and (*b*):

(*a*) 0·1238 gave 0·3271 CO_2 and 0·0776 H_2O. C=72·0; H=6·9.
(*b*) 0·1250 „ 0·3298 CO_2 „ 0·0783 H_2O. C=71·9; H=6·9.
$C_{22}H_{25}O_4N$ requires C=71·9; H=6·8 per cent.

*ψ-Dihydromethyliso**anhydrocryptopine* is sparingly soluble in cold methyl alcohol and not very readily so on boiling; it is also rather sparingly soluble in cold acetone, but dissolves on boiling and separates in groups of glistening needles; it is easily soluble in benzene, even in the cold. The solution of a crystal in a drop of acetic acid gives, with sulphuric acid, a deep orange coloration, which becomes intense port wine on the addition of a drop of dilute nitric acid. A characteristic of the base is its remarkable resistance to reduction, since experiment showed that much remains unchanged after its solution in dilute hydrochloric acid has been boiled with a large excess of sodium amalgam (compare p. 733).

It is also oxidised with unusual difficulty when permanganate is added to its solution in acetone.

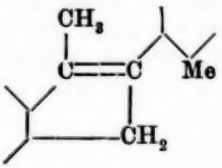
The Methosulphate.—A considerable rise of temperature takes place when methyl sulphate is added to the solution of the base in warm benzene, and the methosulphate begins to separate immediately as a chalky mass. This was collected, washed with benzene, and analysed:

0·1092 gave 0·2332 CO_2 and 0·0626 H_2O. C=58·1; H=6·4.
$C_{22}H_{25}O_4N,Me_2SO_4$ requires C=58·4; H=6·3 per cent.

*ψ-Dihydromethyliso**anhydrocryptopine methosulphate* melts at about 188—190°, and is sparingly soluble in water or methyl alcohol in the cold, but dissolves readily on warming and separates in colourless groups of needles. It is decomposed with some difficulty by boiling methyl-alcoholic potassium hydroxide (15 per cent.), trimethylamine is eliminated, and, on the addition of water, a chalky substance separates, which was not further examined.

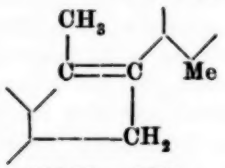
Reduction of the Methosulphate.—When crushed sodium amalgam was added to the cold aqueous solution of the metho-

sulphate at about 50°, the odour of trimethylamine became at once apparent, and a chalky substance separated. After keeping at 50° for some hours, with constant stirring, the precipitate was collected, and found to melt at 160—163°. It was recrystallised from methyl alcohol, in which it was remarkably sparingly soluble, and then melted at 166—167°. That this substance is iso*cryptopidene* (*A*),



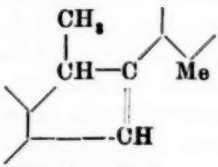
that is to say, is identical with the substance which results from the cold reduction of dihydromethyl*iso*anhydrocryptopine methosulphate (see below), was proved by a comparison of properties, and particularly by the fact that the mixture of the two substances melted at 166—167°.

The iso*Cryptopidenes*, (*A*) *and* (*B*),



(*A*.) M. p. 167°.

and



(*B*.) M. p. 108°.

The difficulty of completely understanding the mechanism of the formation of these curious and interesting substances is referred to in the introduction to this paper (p. 733), and reasons are there given for assigning the above formulæ to the two isomerides.

iso*Cryptopidene* (*A*) (m. p. 167°) is produced by the reduction (i) of the methosulphate of dihydromethyl*iso*anhydrocryptopine, or (ii) of the methosulphate of ψ-dihydromethyl*iso*anhydrocryptopine in alkaline solution and also by the reduction of ψ-dihydromethyl*iso*-anhydrocryptopine in acid solution. The method of formation (ii) has just been described, but the method of preparation which is probably most convenient is that stated under (i). In this reduction, dihydromethyl*iso*anhydrocryptopine methosulphate (2 grams, p. 783), dissolved in water (150 c.c.), is poured on freshly prepared crushed sodium amalgam (100 grams of 3 per cent.) in a porcelain beaker fitted with a mechanical stirrer, and the reduction carried out at a temperature not exceeding 30°. The odour of trimethylamine becomes immediately apparent, and a chalky precipitate of *iso*-

cryptopidene (*A*) gradually forms, but the separation is not complete until the stirring has been continued for two days. The precipitate is then collected, washed with water, and dried in the steam-bath, when it melts at 163—165°, and is almost pure *iso*cryptopidene (*A*), the yield being very good. For analysis, the substance was recrystallised from much methyl alcohol, and considerable difficulty was experienced in obtaining accurate results:

0·1195 gave 0·3231 CO_2 and 0·0654 H_2O. C = 73·7; H = 6·1.
0·1075 „ 0·2901 CO_2 „ 0·0584 H_2O. C = 73·6; H = 6·0.
$C_{20}H_{20}O_4$ requires C = 74·1; H = 6·2 per cent.

iso*Cryptopidene* (*A*) melts at 166—167°, and is remarkably sparingly soluble in boiling methyl alcohol, from which it separates as a sandy powder consisting of well-developed, glistening prisms; it is also very sparingly soluble in boiling alcohol or acetone, and separates from the latter in striated prisms. The solution of a crystal in a few drops of glacial acetic acid gives with sulphuric acid a deep orange coloration, which changes to red on the addition of a drop of nitric acid.

(iii) *The Reduction of ψ-Dihydromethyl*iso*anhydrocryptopine* (p. 784) *in Acid Solution.*—In carrying out this experiment dihydromethyl*iso*anhydrocryptopine (5 grams) (m. p. 122°, p. 782) was dissolved in a large excess of boiling dilute hydrochloric acid, and thus converted into the ψ-isomeride (p. 785). Freshly prepared sodium amalgam (250 grams of 4 per cent.) was then added to the boiling solution, when a small amount of a chalky precipitate separated, which was collected, washed well, and dried in the steam-oven. In this condition, it melted at 162—165°, and, after recrystallisation from methyl alcohol, in which it was very sparingly soluble, at 166—167°. The careful comparison of the properties of this substance with those of the specimen of *iso*cryptopidene (*A*) obtained from the alkaline reduction of dihydromethyl*iso*anhydrocryptopine methosulphate (see above) clearly indicated identity, and this was confirmed by the observation that the mixture of the two preparations melted at 166—167°.

The yield of *iso*cryptopidene (*A*) obtained by reducing ψ-dihydromethyl*iso*anhydrocryptopine in acid solution is only about 8 per cent. of that theoretically possible, and this led to a careful examination of the acid solution which had been separated from the neutral substance by filtration. On the addition of ammonia, a caseous precipitate separated, which soon hardened, and when rubbed with methyl alcohol this yielded a sparingly soluble substance (*a*), which was collected and washed with a little methyl alcohol to remove a readily soluble substance (*b*). The

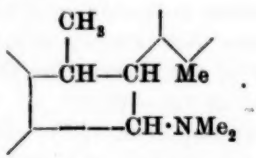
substance (*a*) on fractional crystallisation from methyl alcohol was separated into a small quantity of a new base (m. p. 168—170°) and a considerable quantity (0·8 gram) of unreduced ψ-dihydromethyl*iso*anhydrocryptopine (m. p. 140°). In view of the fact that reduction had been carried out at the boiling point and with a very large excess of amalgam, it is remarkable that so much of this base should have remained unreduced. The base melting at 168—170° is very sparingly soluble in boiling methyl alcohol, from which it separates as a voluminous mass of colourless needles. The solution in acetic acid is coloured yellowish-brown by sulphuric acid, and the addition of a drop of dilute nitric acid changes the colour to brownish-pink:

0·1077 gave 0·2853 CO_2 and 0·0662 H_2O. C = 72·1; H = 6·8.
$C_{22}H_{25}O_4N$ requires C = 71·9; H = 6·8 per cent.

This analysis shows that the base is isomeric with dihydromethyl*iso*anhydrocryptopine (m. p. 122°) and ψ-dihydromethyl*iso*anhydrocryptopine (m. p. 140°), but no evidence is available to explain this isomerism.

The methyl-alcoholic filtrate from the substance (*b*) was mixed with much ether, the ethereal solution washed until quite free from methyl alcohol, dried over potassium carbonate, concentrated, and left in the ice-chest for a week, during which it deposited a small crop of the base melting at 140°, which is practically insoluble in ether.

As no further separation took place on allowing the ether to evaporate in the ice-chest, the base was dissolved in dilute hydrochloric acid and precipitated with ammonia, when a caseous mass separated which, after drying over phosphoric oxide in a vacuum desiccator, gave numbers indicating that the base is *tetrahydromethyliso**anhydrocryptopine*,



0·1139 gave 0·2969 CO_2 and 0·0753 H_2O. C = 71·0; H = 7·5.
$C_{22}H_{27}O_4N$ requires C = 71·5; H = 7·3 per cent.

This base is very readily soluble in the usual solvents, and all attempts to obtain it in a crystalline condition were unsuccessful. The solution in benzene becomes hot on the addition of methyl sulphate, clouds, and a syrup separates which hardens when rubbed with ether. This methosulphate, which is very readily soluble in

water or methyl alcohol, yields a heavy syrup on the addition of boiling potassium iodide to its hot aqueous solution. On remaining in the ice-chest, this gradually deposited nodular crystals, and, when rubbed with methyl alcohol, a considerable quantity of a white, crystalline substance separated, which was collected and recrystallised from methyl alcohol.

Tetrahydromethylisoanhydrocryptopine methiodide melts without effervescence at about 188—190° to a viscid, pale yellow syrup, is comparatively readily soluble in boiling methyl alcohol, but very sparingly so in the cold, and separates well as a glistening mass consisting of thin, flat plates with square ends:

0·1201 gave 0·2390 CO_2 and 0·0641 H_2O. C=54·3; H=6·0.
$C_{22}H_{27}O_4N$,MeI requires C=54·0; H=5·8 per cent.

iso*Cryptopidene* (*B*) (m. p. 108°).—This substance is obtained when the methosulphate of dihydromethyl*iso*anhydrocryptopine (3 grams) (p. 783), dissolved in boiling water (150 c.c.), is treated with sodium amalgam (150 grams of 3 per cent.), care being taken to keep the whole boiling during the operation. Immediately the amalgam is added, a syrupy substance begins to separate, and, if the mass is vigorously stirred, the reduction is finished in a few minutes. The syrupy substance, which crystallises on cooling, is collected and recrystallised from alcohol:

0·1291 gave 0·3497 CO_2 and 0·0701 H_2O. C=73·9; H=6·1.
$C_{20}H_{20}O_4$ requires C=74·1; H=6·2 per cent.

iso*Cryptopidene* (*B*) melts at 108°, is more readily soluble in methyl or ethyl alcohol than the modification (*A*), and separates in groups of glistening needles. It is readily soluble in benzene or acetone in the cold, or in boiling glacial acetic acid, and crystallises particularly well from 70 per cent. acetic acid as a voluminous mass of needles. The solution of a trace in glacial acetic acid gives with sulphuric acid a deep orange-red coloration, which becomes redder on the addition of a drop of dilute nitric acid.

Oxidation.—The solution of the substance (3 grams) in acetone (200 c.c.) is slowly oxidised by the addition of very finely powdered permanganate (5 grams) at the ordinary temperature, the operation requiring about five hours. The manganese precipitate was collected, washed with acetone, extracted with boiling water, and the brown extract concentrated and acidified, when an ochreous precipitate separated in quantity, and was washed and left in contact with porous porcelain until dry. The whole was then dissolved in boiling methyl alcohol and allowed to remain in the ice-chest for two days, when a crystalline acid (0·25 gram) had

separated; this was recrystallised from methyl alcohol, in which it is very sparingly soluble:

0·1060 gave 0·2391 CO_2 and 0·0460 H_2O. C = 61·5; H = 4·9.

$C_{20}H_{20}O_8$ requires C = 61·5; H = 5·1 per cent.

This acid, which may be called *ketohydroxydihydroisocryptopidenic acid*, and the possible constitution of which is discussed on p. 734, is a colourless, satiny mass; it becomes salmon-coloured at 220° and melts at 227° without effervescence.

The solution in concentrated methyl-alcoholic potassium hydroxide becomes pink on boiling, and the colour gradually fades in contact with air.

A trace dissolved in a drop of acetic acid gives with sulphuric acid a deep brown coloration which, on the addition of a drop of dilute nitric acid, gradually fades. The methyl-alcoholic mother liquors of this acid contain a considerable quantity of readily soluble acids, and the acetone extract from the oxidation yields, on evaporation, a small quantity of a yellow syrup, but no attempt was made to identify these mixtures of substances.

The considerable quantities of cryptopine required for this investigation were collected for me by Messrs. T. and H. Smith, of Edinburgh, and I wish again to thank the firm and the managing director, Dr. Alexander Dey, for the generous assistance they have extended to me throughout this inquiry. I am also indebted to Mr. T. V. Barker and Miss M. V. Porter for undertaking the crystallographic measurement of some of the new derivatives. The analyses were again carried out by Mr. Fred Hall with characteristic skill.

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LXI.—*The Freezing Point of Solutions, with Special Reference to Solutions Containing Several Solutes.*

By CHARLES EDWARD FAWSITT.

IN proceeding to use freezing-point determinations for the estimation of certain ingredients in liquids containing an unlimited number of ingredients, the author found that it was necessary to consider rather closely the freezing points of solutions. In particular, for the purpose in question, it was necessary to consider

how the calculated molecular depression of the freezing point of a solvent by a solute is dependent on the concentration of the solute (Part I), and it was necessary further to consider what effect is produced on the freezing point of a solvent by several solutes used together, as compared with the effect of these solutes used separately (Part II).

These two matters are considered in this paper.

Part I.

The Effect of Concentration of Solute in Freezing-point Determinations.

The freezing point of a solvent is usually lowered by dissolving any substance in it, and for very dilute solutions the depression of the freezing point, (Δ), is proportional to n/N, where n is the number of solute molecules and N is the number of solvent molecules.

This proportionality is proved from theoretical considerations, but holds only for excessively dilute solutions. For solutions of a concentration of, say, 1—10 per cent. of solute, Δ is not strictly proportional to n/N, and it has been suggested that the formula

$$\Delta \propto \frac{n}{N+n}$$

should be used instead of

$$\Delta \propto \frac{n}{N}.$$

Taking the first formula, which is more commonly used,

Let w = weight in grams of solute,
m = molecular weight of solute,
W = weight of solvent in grams,
M = molecular weight of solvent,

$$\Delta \propto \frac{w}{m} \times \frac{M}{W},$$

or

$$\Delta = K \times 1000 \times \frac{w}{m} \times \frac{1}{W} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where K is a constant (the van't Hoff constant) for the solvent and represents the depression caused by introducing one gram-molecular weight of solute into 1000 grams of solvent.

Equation (1) is usually employed in making freezing-point calculations, more especially where these are used in determining molecular weights of solutes.

It is observed that when the depressions Δ_1, Δ_2, Δ_3, corresponding with several weights of solute, w_1, w_2, w_3, are determined, the molecular weight of the solute, calculated according to equation (1), is often not constant, even with non-associated or non-dissociated solutes. In such cases, the numbers more often tend to rise than to fall.

It might be thought that by using the formula

$$\Delta \propto \frac{n}{N+n}$$

instead of

$$\Delta \propto \frac{n}{N},$$

better results would be obtained.

Now

$$\Delta \propto \frac{n}{N+n}$$

leads to

$$\Delta \propto \frac{M \,.\, w}{[m \,.\, W + wM]},$$

or

$$\Delta = K \times 1000 \,.\, \frac{w}{m[W + w/m \,.\, M]} \quad . \quad . \quad . \quad . \quad (2)$$

where K is the same constant as in (1). The application of equation (2) to the calculation of molecular weights instead of (1) is not attended by satisfactory results.

In particular, it cannot be made to serve any useful purpose when the molecular weights, calculated according to (1), decrease as the concentration rises, a case which sometimes occurs.

If, however, instead of the expression in (2) we use the formula

$$\Delta = \frac{K \times 1000 \times w}{m[W + bw]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where b is an arbitrarily introduced constant dependent on solute and solvent, not necessarily equal to M/m, and, indeed, sometimes negative, the results obtained are satisfactory.

Abegg (*Zeitsch. physikal. Chem.*, 1894, **15**, 209) tried the equation

$$\Delta = \frac{K \times n \times 1000}{W} + B\left(\frac{n}{W}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where K is the ordinary van't Hoff constant as used in equation (1), and should be the same for all solutes in any particular solvent, whilst B is an arbitrary constant which varies with the solute. The application of this formula (4) certainly gives better results

in many cases than (1) or (2), but is not so simple a formula as (3). The latter gives quite as good results as (4) both for solutions containing a single solute and solutions containing several solutes.

The author considers that formula (3) is the most suitable for adoption in freezing-point calculations.

The constant b in equation (3) can be calculated from two observations; if w_1 and w_2 be two different weights of a solute giving depressions Δ_1 and Δ_2 with a particular solvent, then

$$b = \frac{W(\Delta_1/w_1 - \Delta_2/w_2)}{\Delta_2 - \Delta_1}.$$

The constant B in equation (4) can also be calculated from two observations,

$$B = \frac{W^2(\Delta_1/w_1 - \Delta_2/w_2)}{w_1 - w_2}.$$

In the following tables, m is the (theoretical) molecular weight, m' is the molecular weight as calculated by the equation

$$m' = \frac{K \,.\, 1000 \,.\, w}{\Delta \,.\, W} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

m'' is the molecular weight as calculated by the equation

$$m'' = \frac{K \,.\, 1000 \,.\, w}{\Delta \,.\, [W + bw]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

m''' is the molecular weight as calculated by the equation

$$m''' = \frac{K \,.\, 1000 \,.\, w}{W[\Delta - B \,.\, w^2/W^2]} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which is derived from equation (4).

From tables I, II, III, and IV it will be seen that m'' is fairly constant whether m' rises or falls with increasing concentration of solute.

In table II, m''' is also given, and it will be seen that it is just as constant as m'', but not more so.

Table I.

Solute, Ethyl Ether, $m = 74$; Solvent, Cineole.
$W = 18{\cdot}27$, $b = 1{\cdot}53$, $K = 6{\cdot}7$.

Grams of solute in 100 grams of solvent.	Δ.	m' (calculated).	m''.
0·707	0·624	76·0	75·1
1·48	1·275	77·6	75·9
2·2	1·875	78·5	76·0
3·4	2·874	79·3	75·2
5·15	4·255	81·0	75·1

TABLE II.

Solute, l-α-*Phellandrene*, $m=136$; *Solvent*, *Benzene*.
$B=-33{\cdot}6$, $W=18{\cdot}47$, $b=0{\cdot}87$, $K=5{\cdot}0$.

$w\times100/W$.	Δ.	m'.	m''.	m'''.
0·96	0·356	135·2	133·9	133·9
2·12	0·778	136·5	133·9	133·7
3·32	1·194	138·9	134·9	134·6
4·7	1·685	140·4	134·7	134·3
6·24	2·209	141·2	133·8	133·1
7·34	2·559	143·3	134·7	133·8

The variations in m'' (and m''') of the tables are not greater than the experimental errors.

Tables of this kind could be multiplied indefinitely.

Tables III and IV give examples where b has a negative value (that is, where the molecular weight as calculated from equation (1) falls with increasing concentration). Table III has been calculated from data given by Abegg (*loc. cit.*).

TABLE III.

Solute, Ethyl Alcohol; Solvent, Water.
$K=1{\cdot}86$, $W=100$, $m=46$, $b=-0{\cdot}5$.

w.	Δ.	m'	m''
8·10	3·215	46·8	48·8
10·75	4·35	46·0	48·6
13·81	5·605	45·8	49·2
17·79	7·49	44·6	49·2
22·50	9·705	43·1	48·5
32·68	15·09	40·2	48·1

TABLE IV.

Solute, Sucrose; Solvent, Water.
$K=1{\cdot}86$, $W=100$, $m=342$, $b=-0{\cdot}26$.

w.	Δ.	m'	m''
0·973	0·053	341·4	342·3
2·231	0·123	337·4	339·3
4·276	0·237	335·6	339·4
8·550	0·481	330·7	338·2
17·292	0·989	325·1	340·2

In table III it will be seen that m'' is constant within the experimental error up to a concentration of 32·68 per cent. of solute.

Table IV is calculated from data given by Raoult (1898).

When the molecular weight as calculated according to equation (5) rises with increasing concentration, this is due probably (i) to the volume of the solution becoming continually greater than the volume of the solvent, or (ii) to association of the solute molecules.

When the molecular weight as calculated according to (5) falls with increasing concentration, this is due probably to combination between solute and solvent.

Whatever be the cause of the rising or falling of the calculated molecular weight, there seems to be little doubt that where the molecular weight calculated according to (5) rises or falls with

change of concentration, formula (6) gives values for m'' constant to about 1 per cent. This is, then, the calculated value of the molecular weight for very small concentrations. It does not immediately follow that this constant value (m'') represents accurately the true molecular weight (m), for there are other abnormalities noticed in the results of freezing-point measurements besides the rising and falling of the (calculated) molecular weight. The molecular weight as calculated for small concentrations may be higher or lower than the true molecular weight. It is higher in the case of many solutes showing association, for example, ethyl alcohol dissolved in cineole. It is also sometimes lower than the true molecular weight; this is more particularly noticeable in the case of some terpenes dissolved in benzene and in cineole.

Part II.

Freezing Point of a Mixture of Solutes Dissolved in a Solvent.

In proceeding to the case of several solutes dissolved together in a solvent, it will be desirable to eliminate certain complications. For example, it is not desirable to use as solutes in the mixture, (i) such solutes as exhibit association or dissociation in solution, (ii) such as will form mixed crystals with the solvent, (iii) such as will combine with the solvent or with each other.

In some cases, a fairly close agreement is observed between the depression of the freezing point, caused by a mixture of solutes, and the sum of the depressions, caused by the ingredients when introduced by themselves (separately) into the solvent.

Table V.

Solvent, Benzene; Solute, Toluene.

$W = 18{\cdot}65$, $K = 5{\cdot}0$.

W	Percentage of solute.	Δ.
0·1822	0·98	0·542
0·3522	1·89	1·017
0·6866	3·68	2·028

Table VI.

Solvent, Benzene; Solute, p-*Xylene.*

$W = 15{\cdot}092$, $K = 5{\cdot}0$.

w	$w \times 100/W$.	Δ.
0·2306	1·53	0·750
0·5224	3·46	1·626
0·8151	5·40	2·542

In table VII and the following tables, Δ_1 is the depression of the freezing point of a mixture of solutes in a solvent obtained by adding together the calculated depressions of the freezing point caused by each ingredient. Δ is the observed depression.

TABLE VII.

Solvent, Benzene; Solute, a Mixture containing 84·7 *per cent. of Toluene and* 15·3 *per cent. of* p-*Xylene.*

$W = 15{\cdot}29.$

w.	Δ.	Δ_1.
0·1887	0·670	0·648
0·3663	1·274	1·268
0·615	2·114	2·139

The calculated and observed depressions do not differ by much more than the experimental errors in this case.

However, if a considerable number of cases are examined, using various solutes and solvents, it will be found that there is often a considerable discrepancy between the values of Δ and Δ_1, especially at large concentrations; sometimes Δ is greater than Δ_1, sometimes less. This is, however, only to be expected from equation (3).

From equation (3) we are led to believe that, instead of using W, the weight of pure solvent, in our calculations, we should use $W + bw$.

Consider now two solutes, P and Q, having molecular weights m_p and m_q; let w_p grams of P be dissolved in a solvent, giving a depression Δ_p; let w_q grams of Q when dissolved (separately) in the solvent give a depression Δ_q.

Then the separate depressions are:

$$\Delta_p = \frac{K \,.\, 1000 \,.\, w_p}{m_p \,.\, [W + b_p w_p]} \quad \text{and} \quad \Delta_q = \frac{K \,.\, 1000 \,.\, w_q}{m_q [W + b_q w_q]},$$

and the sum

$$\Delta_p + \Delta_q = K \,.\, 1000 \left\{ \frac{w_p/m_p}{[W + b_p w_p]} + \frac{w_q/m_q}{[W + b_q w_q]} \right\} \quad . \quad (8)$$

The sum $\Delta_p + \Delta_q$ differs from the observed value Δ_{p+q}, since the observed value would be expected to be given by

$$\Delta_{p+q} = \frac{K \,.\, 1000 \{w_p/m_p + w_q/m_q\}}{[W + b_p w_p + b_q w_q]} \quad . \quad . \quad . \quad . \quad (9)$$

If b_p and b_q are positive, then Δ_{p+q} will be less than $\Delta_p + \Delta_q$. If b_p and b_q are negative, then Δ_{p+q} will be greater than $\Delta_p + \Delta_q$. We may say then, in general, that on mixing two solutes the molecular weights of which when calculated according to the usual formula (equation 5) rise with increasing concentration ($b + w$), we should expect that the actual depression produced by the two

together would be less than the sum of the depressions produced by each solute separately.

If, on the other hand, the molecular weights when calculated according to equation (5) decrease with increasing concentration (b negative), we should expect that the depression produced by two solutes together would be greater than the sum of the depressions of the separate solutes.

An examination of a considerable number of cases shows that, qualitatively, these statements are borne out by facts.

It is assumed, of course, in such cases that there is no combination between the various solutes. This would itself have the effect of making the observed less than the calculated depression.

Below are given the results of a number of freezing-point determinations on single solutes in benzene showing how the molecular weight, calculated according to equation (5), alters with change of concentration, and, subsequently, tables showing the results obtained from mixtures of some of these solutes in benzene.

Results for mixtures of solutes are given for the three solvents benzene, nitrobenzene, and water.

Δ_2 in the following tables denotes the calculated depression as obtained from equation (9).

m' is calculated from equation (5).

Percentage of solute means weight of solute in 100 grams of solvent.

Benzene as Solvent.

The following results were obtained with individual solutes.

TABLE VIII.

Solvent, Benzene; Solute, Toluene.

$K=5$, $m=92$.

Percentage weight of solute.	Δ.	m'.
1·467	0·847	86·6
3·088	1·754	88·1
4·715	2·588	91·1
6·205	3·338	93·0
7·803	4·148	94·1

b Calculated from these figures is 1·312.

TABLE IX.

Solvent, Benzene; Solute, m-*Xylene.*

$m=106$.

Percentage weight of solute.	Δ.	m'.
1·189	0·568	104·7
2·674	1·253	106·7
4·111	1·881	109·3
5·595	2·526	110·8
6·773	3·014	112·4

b Calculated from these figures is 1·339.

TABLE X.

Solvent, Benzene; Solute, d-Pinene.

$m = 136$.

Percentage.	Δ.	m'.
1·411	0·54	130·6
2·823	1·032	136·9
4·438	1·564	141·9
6·193	2·15	144·1

b Calculated from observations (1) and (4) is 2·21.

TABLE XI.

Solvent, Benzene; Solute, α-Phellandrene.

$m = 136$.

Percentage.	Δ.	m'.
0·962	0·356	135·2
2·123	0·778	136·5
3·316	1·194	138·9
4·731	1·685	140·4
6·236	2·209	141·2
7·335	2·559	143·3

b Calculated from observations (1) and (6) is 0·87.

TABLE XII.

Solvent, Benzene; Solute, Cineole.

$m = 154$.

Percentage.	Δ.	m'.
1·046	0·350	149·4
2·708	0·870	155·7

b Calculated from observations (1) and (2) is 2·59.

TABLE XIII.

Freezing-point Determinations with more than One Solute in Benzene as Solvent. Solvent, Benzene ($K = 5·0$).

No.	Solute.	Value of "*b*" for solute.	Percentage weight of solute.	Δ.	Δ_1.	Δ_2.	Percentage difference between Δ and Δ_2.
1	Toluene	1·312	2·368	1·569	1·604	1·588	1·2
	m-Xylene ...	1·339	0·532				
2	Toluene	1·312	3·759	2·469	2·508	2·466	−0·1
	m-Xylene ...	1·339	0·845				
3	Toluene	1·312	4·764	3·299	3·442	3·334	1·1
	m-Xylene ...	1·339	1·708				
4	Cineole	2·59	4·107	1·881	2·047	1·930	2·7
	d-Pinene ...	2·21	1·068				
	Phellandrene	0·87	0·944				
5	Cineole	2·59	1·571	1·832	1·943	1·824	−0·5
	d-Pinene ...	2·21	2·025				
	Phellandrene	0·87	1·790				

Nitrobenzene as Solvent.

Nitrobenzene is similar as a solvent to benzene in that the value of *b* for solutes in nitrobenzene was positive in all cases experi-

mented on. The molecular weight (m') of single solutes dissolved in nitrobenzene, if calculated according to equation (5), rises with increasing concentration. The results for the individual solutes are omitted here, but the results for several solutes dissolved together in nitrobenzene are given in table XIV.

As in the case of benzene, the sum of the individual depressions is always greater than the depressions obtained for the solutes when dissolved together.

The corrected calculated value (Δ_2), using the b correction as per equation (9), is, however, as with benzene, much nearer to the observed value.

TABLE XIV.

Freezing-point Determinations with more than One Solute in a Common Solvent. Solvent, Nitrobenzene ($K=7\cdot0$).

No.	Solute.	Value of "b" for solute.	Percentage weight of each solute.	Δ.	Δ_1.	Δ_2.	Percentage difference between Δ and Δ_2.
1	Toluene.....	2·295	0·926	2·439	2·534	2·463	+1
	Benzene ...	2·36	2·048				
2	Toluene ...	2·295	1·624	4·070	4·314	4·117	+1·1
	Benzene ...	2·36	3·587				
3	Toluene.....	2·295	2·401	2·800	2·929	2·820	+0·7
	m-Xylene	1·138	0·861				
	Benzene ...	2·36	0·591				
4	Toluene.....	2·295	3·919	4·323	4·671	4·399	+1·7
	m-Xylene ...	1·138	1·404				
	Benzene ...	2·36	0·964				
5	Toluene.....	2·295	2·574	3·599	3·883	3·672	+2·0
	m-Xylene ...	1·138	0·578				
	Benzene ...	2·36	1·750				

Water as Solvent.

In this case, it was not thought necessary to carry out any experimental work, as sufficient material for calculation may be obtained in the literature dealing with freezing points.

Using Abegg's numbers (*loc. cit.*), it is found that b is sometimes negative for solutes in aqueous solutions.

The values for b have been calculated for a number of solutes, and the results in table XV give the observed and calculated values for mixtures of these solutes.

TABLE XV.

Freezing-point Determinations with more than One Solute in a Common Solvent. Solvent, Water.

No.	Solute.	Value of "b" for solute.	Percentage weight of solute.	Δ.	Δ_1.	Δ_2.	Percentage difference between Δ and Δ_2.
1	Glycerol ...	−0·284	5·235	2·145	2·057	2·119	−1·3
	Sucrose ...	−0·24	16·857				
2	Glycerol ...	−0·284	10·90	3·48	3·294	3·431	−1·4
	Sucrose ...	−0·24	17·54				
3	Alcohol ...	−0·463	3·924	3·47	3·320	3·395	−2·1
	Glycerol ...	−0·284	8·64				
4	Alcohol ...	−0·463	5·474	4·13	4·058	4·074	−1·4
	Acetone.....	0·235	6·251				
5	Alcohol	−0·463	5·934	6·55	6·393	6·437	−1·7
	Acetone.....	0·235	13·555				

It will be noticed that for the solutes and solvents considered, and in spite of the corrected method of calculation employed when several solutes are used together, an error of as much as 2 per cent. occurs in some cases. This error is sometimes positive and sometimes negative, and may be due, (i) to reaction between the various solutes, or (ii) to action of the solute on the solvent, or (iii) to experimental errors in determining the freezing point of the solutions.

When freezing-point determinations are to be used for purposes of analysis, these errors have to be taken into account. Before the method can be applied directly to a given sample, the errors of determination must have been ascertained by experiments on somewhat similar material.

Summary.

(1) In freezing-point determinations, there may with advantage be substituted for W, the weight of solvent, the expression $W + bw$, where w is the weight of the solute and b is a constant which depends both on the solute and the solvent, and is at present determinable only by experiment with the solute and solvent.

(2) When several solutes are dissolved at one time in the same solvent, then, if b is positive for the individual solutes, the sum of the individual depressions of the freezing point by the various solutes is greater than the observed depression of the freezing point; if b is negative for each individual solute, the sum of the

individual depressions is less than the observed depression of the freezing point.

(3) If several solutes are dissolved together in a solvent and the quantity of solvent be taken as $W + w_1b_1 + w_2b_2 + w_3b_3 +$, where W is the actual weight of the solvent, and w_1, w_2, w_3 are the weights of the solutes, and b_1, b_2, b_3 are the values of the constant b for each solute, as explained in paragraph (1) above, then the sum of the calculated values of the depressions of the individual solutes differs from the observed total depressions by only a small error in all cases considered by the author.

I desire to thank Mr. C. H. Fischer for carrying out the experimental work described in this paper.

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LXII.—*The Use of Freezing-point Determinations in Quantitative Analysis.*

By CHARLES EDWARD FAWSITT.

CONSIDERABLE use has been made of freezing-point determinations as an aid to analytical work in recent years.

The freezing point of a liquid like milk or blood serum has been used as a characteristic for these substances independently of what the constituent solutes are.

Fox and Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842) have made use of a determination of the freezing point to obtain the percentage of phenol in commercial cresylic acid. There is a little uncertainty in using the freezing-point results in such a case, because the other substances in crude cresylic acid, namely, the three cresols, have all the same molecular weight.

Weiss and Downs (*ibid.*, 863) show that the percentage of phenol in tar oils may be determined by a freezing-point determination provided a density determination of the mixture is also carried out.

Drapier (*Compt. rend.*, 1915, **161**, 461) has suggested that the percentage of one ingredient A_1 in a mixture A could be obtained provided that one knows the lowering of the freezing point by the mixture A (solute) when dissolved in A_1 (solvent), and also when A is dissolved in some other solvent, S, which is not an ingredient of A. Drapier, however, has apparently not followed up this

suggestion by publishing any experimental support for the method. It seemed to the author, however, that this method was worth while investigating.

Theoretical.—Let us suppose that the depression of freezing point produced by dissolving a solute in a solvent is (1) proportional to the concentration of the solute, (2) inversely proportional to the molecular weight of the solute if equal weights of different solutes are compared; let us suppose, further, (3) that a solute exercises its usual effect in depressing the freezing point of a solvent independently of the presence or absence of other solutes.

Conditions (1) and (2) are approximately true for most dilute solutions. The effect of one solute on the depression of the freezing point of a solvent, when another second solute is present (3), has not yet been very thoroughly investigated, but in several investigated cases (3) certainly does not hold quite true even in dilute solution (see preceding paper). In developing the theory of this process it will, however, be assumed in the first instance that (1), (2), and (3) hold good. Consider a liquid mixture A. The mixture A is made up of several ingredients, A_1, A_2, A_3, A_4, etc. . . . An. It is required to find out the percentage of the ingredient A_1. The ingredient A_1 must be such that it is capable of being frozen at a convenient temperature.

Obtain also a solvent, S, in which A is completely soluble; S must also be a substance (liquid) which can be frozen at a convenient temperature.

A small quantity, a, of the substance A is dissolved in P grams of the solvent S, and the depression in the freezing point of S noted. Call this Δ_s. Also a quantity of the mixture A, say b grams, is dissolved in Q grams of the solvent A_1, and the depression in the freezing point of $A_1 = \Delta_{A_1}$ noted.

Further, let $a = a_1 + a_2 + a_3 + a_4 \ldots$, where a_1, a_2, etc., are the weights of the several ingredients A_1, A_2, etc., in a; let $b = b_1 + b_2 + b_3 + b_4 \ldots$, where b_1, b_2, etc., are the weights of the ingredients A_1, A_2, etc., in b; let K_1 = the cryoscopic constant for the solvent, S, that is, the depression produced in the freezing point of S by dissolving in 1000 grams of S one gram-molecular weight of any solute; let K_2 = the cryoscopic constant for the solvent A_1; let m_1, m_2, m_3 . . . be the molecular weights of the constituents A_1, A_2, A_3 . . ., then

$$\Delta_s = \frac{1000\,K_1}{P}\left(\frac{a_1}{m_1} + \frac{a_2}{m_2} + \frac{a_3}{m_3} + \ldots\ldots\right) \quad (1)$$

and

$$\Delta_{A_1} = \frac{1000\,K_2}{Q + b_1}\left(\frac{b_2}{m_2} + \frac{b_3}{m_3} + \ldots\ldots\right) \quad (2)$$

Now if $a/b = r$, (2) becomes

$$\Delta_{A_1} = \frac{1000\ K_2}{(Q+b_1)r} \cdot \left(\frac{a_2}{m_2} + \frac{a_3}{m_3} + \ldots\ldots\right) \quad . \quad . \quad . \quad (3)$$

Multiplying equation (1) by $\frac{K_2}{(Q+b_1)r}$, and (3) by $\frac{K_1}{P}$, we get

$$\frac{K_2\Delta_s}{(Q+b_1)r} - \frac{K_1\Delta_{A_1}}{P} = \frac{K_1K_2 \times 1000}{P\,.\,(Q+b_1)\,.\,r} \cdot \frac{a_1}{m_1}$$

$$\therefore a_1 = \frac{m_1(K_2\Delta_s P - K_1\Delta_{A_1} rQ)}{K_1(1000\ K_2 + m_1\Delta_{A_1})} \quad . \quad . \quad . \quad . \quad (4)$$

It has, however, been pointed out (see preceding paper) that in dealing with ordinary concentrations, the weights of solvent should not be taken as P and $(Q+b_1)$, but that these values should be corrected by the addition of a term depending on the weight of solute present. P would then become

$$P + \delta_1 a_1 + \delta_2 a_2 + \delta_3 a_3 + \delta_4 a_4 + \ \ldots,$$

where δ_1, δ_2, δ_3 . . . are constants for each ingredient of the solute $= P + \delta a$, where δ is the average value of the constants δ_1, δ_2, δ_3, δ_4 for the several ingredients of the solute A. Similarly, $Q + b_1$ would become $Q + b_1 + \gamma(b_2 + b_3 + b_4 + \ \ldots)$, where γ is the average value of the correction factor for the solutes A_2, A_3, A_4, A_5, etc.

Formula (4) then becomes

$$a_1 = \frac{m_1[K_2\Delta_s(P+\delta a) - K_1\Delta_{A_1}\{Q + \gamma(b-b_1)\}r]}{K_1(1000\ K_2 + m_1\Delta_{A_1})} \quad . \quad . \quad (5)$$

It may be wondered how the value for b_1 can be obtained for insertion in this formula (5). To obtain this, a calculation of a_1 is first made, using formula (4). Then $b_1 = a_1/r$. This value, which is only roughly, but yet sufficiently, accurate is used for a more accurate determination of a_1, according to equation (5).

The values of δ and γ can be obtained directly from the experiment used in determining a_1.

In many cases it will be necessary to introduce a further correction in the formula. It has already been pointed out in the preceding paper that the depression of freezing points caused by a number of solutes in one solvent is somewhat different from the expected value even after due allowance has been made by the correction in the amount of solvent as used in obtaining equation (5) from equation (4).

The values of Δ_s and Δ_{A_1} should, then, be corrected further by an amount which can only be determined by previous experiment on the class of solute which is under investigation.

Let us use the correction factors (constants) U and V for Δ_s and Δ_{A_1}.

The percentage of A_1 in A is then

$$\frac{100 \cdot m_1[K_2\Delta_s U(P+\delta a) - K_1\Delta_{A_1}\{Q+\gamma(b-b_1)\}rV]}{a \cdot K_1[1000K_2+\Delta_{A_1}m_1]} \quad (6)$$

Another correction which must sometimes be introduced is due to the fact that when A_1 is dissolved in the solvent S, the calculated molecular weight may not be exactly m_1, but some other value, say m'_1. This value, if appreciably different from m_1, should be substituted for m_1. The formula to be used is then: percentage of

$$A_1 = \frac{100 \cdot m_1'[K_2\Delta_s U(P+\delta a) - K_1\Delta_{A_1}\{Q+\gamma(b-b_1)\}rV]}{aK_1[1000K_2+\Delta_{A_1}m_1']} \quad (7)$$

In considering what estimations the method might usefully be applied to, the author thought that the determination of (*a*) benzene in light coal-tar oils was a suitable case, also (*b*) the determination of cineole in eucalyptus oils. With regard to (*a*), the determination of benzene can be obtained approximately (1) by distillation, (2) sometimes by direct determination of the freezing point, especially after addition of extra benzene, (3) by nitration, with subsequent determination of the products, but the method at present under discussion would sometimes be found more suitable.

With regard to the determination of cineole in eucalyptus oils, the phosphoric acid method, although fairly satisfactory as a rule, requires a comparatively large quantity of oil (10 grams). The resorcinol method has been used a good deal lately by H. G. Smith, but he has informed the author that in certain cases it is not trustworthy.

In the following experiments, as ordinary "Beckmann" type of thermometer graduated to 0·01° was used.

Estimation of Benzene in Mixtures.

The mixtures were used as solutes in depressing the freezing point of nitrobenzene and of benzene.

K_2 for benzene = 5·0; K_1 for nitrobenzene = 7·0.

The results were calculated according to the formula: percentage of benzene =

$$\frac{100 \times 78[5 \cdot \Delta_s \cdot (P+2{\cdot}3a) \cdot 1{\cdot}018 - 7 \cdot \Delta_{A_1} \cdot \{Q+1{\cdot}4(b-b_1)\} \cdot 1{\cdot}008 \cdot r]}{a \cdot 7 \cdot [5000+\Delta_{A_1} \cdot 78]}$$

Mixture A.

The composition of the mixture was: benzene 68·85, toluene 31·15 per cent.

TABLE I.

Freezing-point Determinations in Nitrobenzene as Solvent.

No.	Percentage of solute.	Δ_2.
1	1·010	0·86
2	2·159	1·819
3	2·974	2·439
4	4·070	3·266
5	5·211	4·07

TABLE II.

Solvent, Benzene.

No.	Percentage of solute.	ΔA_1.
1	1·580	0·30
2	3·941	0·702
3	6·541	1·130
4	9·22	1·550
5	11·88	1·920

TABLE III.

Calculation of Percentage of Benzene in Mixture A.

Observations used.		Percentage calculated.
Table I.	Table II.	
No. 1	No. 2	69·6
3	3	70·2
5	5	70·4

Mixture B.

The composition of the mixture was: benzene 15·3, toluene 62·4, *m*-xylene 22·3 per cent.

TABLE IV.

Solvent, Nitrobenzene.

No.	Percentage of solute.	Δ_2.
1	1·383	1·040
2	2·589	1·909
3	3·853	2·800
4	5·273	3·691
5	6·287	4·323

TABLE V.

Solvent, Benzene.

No.	Percentage.	ΔA_1.
1	1·392	0·642
2	3·131	1·438
3	4·844	2·169
4	6·409	2·789
5	7·734	3·299

TABLE VI.

Calculation of Percentage of Benzene in Mixture B.

Observations used.		Percentage calculated.
Table IV.	Table V.	
No. 1	No. 1	14·1
2	2	13·4
3	3	14·9
4	4	15·0

Mixture C.

The composition of the mixture was: benzene 10·00, toluene 61·48, *m*-xylene 9·19, o-xylene 8·56, *p*-xylene 9·06, thiophen 1·71 per cent.

TABLE VII.

Solvent, Nitrobenzene.

No.	Percentage of solute.	Δ_s.
1	1·193	0·898
2	2·302	1·684
3	3·627	2·577

TABLE VIII.

No.	Percentage of solute.	Δ_{A_1}.
1	1·488	0·737
2	2·925	1·417
3	4·248	1·980

TABLE IX.

Calculation of Percentage of Benzene in Mixture C.

Observations used.		Percentages calculated.
Table VII.	Table VIII.	
1	1	8·3
3	3	10·2

Estimation of Cineole in Mixtures.

The mixtures were made of cineole, pinene, and *l*-α-phellandrene. The mixtures were used as solutes in depressing the freezing points of benzene and of cineole.

K_1 for benzene = 5·0; K_2 for cineole = 6·7.

The results were calculated according to the formula: percentage of cineole =

$$\frac{100 \times 146[6{\cdot}7 \,.\, 1{\cdot}02 \,.\, \Delta_s \,.\, (100 + 1{\cdot}7a) - 5{\cdot}0 \times 1{\cdot}04 \,.\, \Delta_{A_1} \,.\, \{100 + 1{\cdot}7(b - b_1)r]}{a \,.\, 5[6700 + \Delta_{A_1} \,.\, 146]}$$

It will be noticed that 146 (obtained by experiment) was used for the molecular weight of cineole in benzene, instead of 154, the theoretical value.

Mixture D.

The composition of the mixture was: cineole 67·1, pinene 17·5, phellandrene 15·4 per cent.

TABLE X

Solvent, Benzene.

No.	Percentage of solute.	Δ_s.
1	1·887	0·642
2	3·948	1·313
3	5·759	1·881

TABLE XI.

Solvent, Cineole.

No.	Percentage of solute.	Δ_{A_1}.
1	3·59	0·568
2	8·20	1·262
3	13·72	2·051

TABLE XII.

Calculation of Percentage of Cineole in Mixture D.

Observations used.		
Table X.	Table XI.	Percentage calculated.
1	1	67·2
2	2	68·5
3	3	67·8

Mixture E.

The composition of the mixture was: cineole 29·2, pinene 37·6, phellandrene 33·2 per cent.

TABLE XIII.

Solvent, Benzene.

No.	Percentage of solute.	Δ_p.
1	1·786	0·633
2	3·57	1·244
3	5·39	1·832

TABLE XIV.

Solvent, Cineole.

No.	Percentage of solute.	ΔA_1.
1	1·48	0·518
2	3·957	1·356
3	6·63	2·210

TABLE XV.

Calculation of Percentage of Cineole.

Observations used.		
Table XIII.	Table XIV.	Percentage calculated.
1	1	28·4
2	2	28·1
3	3	29·4

Mixture F.

The composition of the mixture was: cineole 54·3, pinene 24·3, phellandrene 21·4 per cent.

TABLE XVI.

Solvent, Benzene.

No.	Percentage of solute.	Δ_p.
1	1·708	0·599
2	3·596	1·219

TABLE XVII.

Solvent, Cineole.

No.	Percentage of solute.	ΔA_1.
1	2·124	0·479
2	7·580	1·655

TABLE XVIII.

Calculation of Percentage of Cineole in Mixture F.

Observations used.		
Table XVI.	Table XVII	Percentage calculated.
1	1	55·0
2	2	52·9

From these results, it will be seen that the calculation yields figures which are within about 2 units of the true percentage. This error is completely accounted for by errors of experiment, more particularly the reading of the thermometer. It is not possible to be sure that the calculated percentage is any nearer to the true result than this, using the Beckmann freezing-point apparatus in the ordinary way. As unknown mixtures might in some cases contain unknown ingredients, it would be impossible, unless with previous experience with similar mixtures, to know the values of U and V in equation (7), and any tentative value used for U or V might result in a rather large error in the calculated percentage. In certain cases of this kind experimented on, the error in the percentage was as high as 8 units. The error is stated above as so many units, because in the formula (7), for the calculation of the percentage of A_1, one term containing Δ_{A_1} is subtracted from another containing Δ_s, giving a number which varies directly as the final result (percentage of A_1). It is not therefore possible to express the error of experiment as a percentage.

Summary.

The method of estimating an ingredient A_1 in a substance A by finding the freezing-point depression of A in A_1 (as solvent), and also in some other solvent, S, may be applied in special cases where it is possible to experiment previously with samples of substance somewhat similar to A. The percentage of A_1 can then be determined in certain cases to an accuracy of about two units with the ordinary freezing-point apparatus.

When it is not possible to experiment with the same class of substance beforehand, the method of determination is liable to give a result with a much larger error. The method can therefore only be recommended when (1) there has been previous experience with the same class of substance, or (2) when other possible methods of determination are not capable of a greater degree of accuracy, or (3) where other methods require for their successful application a larger quantity of substance than is available. The freezing-point method already described requires for its successful application about 1 gram of substance, but it is more satisfactory if a larger amount, say 4—6 grams, is available.

I wish to thank Mr. C. H. Fischer for carrying out the experimental work in this paper.

CHEMICAL DEPARTMENT,
UNIVERSITY OF SYDNEY. [*Received, April 14th*, 1919.]

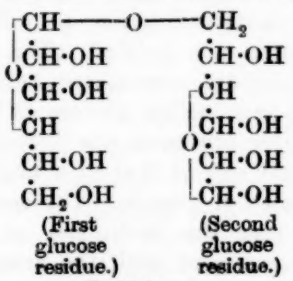
LXIII.—*The Constitution of the Disaccharides. Part III. Maltose.*

By Walter Norman Haworth and Grace Cumming Leitch.

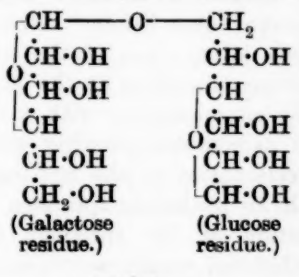
Maltose is a reducing sugar which yields, on hydrolysis with dilute acid or with the enzyme maltase, two molecular proportions of glucose. Consequently, it is regarded as a biose having the reducing group of one glucose molecule united through an anhydride linking with a second glucose residue. Confirmation of this view is found in the oxidation of maltose to maltobionic acid, which gives rise on hydrolysis to glucose and gluconic acid (Fischer and Meyer, *Ber.*, 1889, **22**, 1941).

No evidence has hitherto been available indicating which of the hydroxyl groups of the second glucose residue is involved in this union (see formula I). The present authors have shown in Part II of this series of communications (T., 1918, **113**, 188) that in lactose the reducing group of the galactose residue is linked with the hydroxyl group of the penultimate carbon atom of the glucose molecule. The possibility that this mode of linking was present also in maltose appeared improbable in view of Hudson's observation (*J. Amer. Chem. Soc.*, 1916, **38**, 1566) that lactose exhibits a close parallelism with cellobiose and not with melibiose, to which a different constitution has been assigned (Haworth and Leitch, *loc. cit.*). There was, however, no definite ground for excluding this possibility in the case of maltose, nor, indeed, for assuming that any one hydroxyl group attached to the third, fifth, or sixth carbon atom from the reducing end of the second glucose chain could not equally well be concerned in the union of the two molecules of the hexose.

In the course of the present investigation, this uncertainty has been removed, and it has been shown that maltose must have the constitution indicated below, and thus corresponds structurally,



(I) Maltose.



Melibiose.

among the diglucose disaccharides, with melibiose of the glucose–galactose class.

This constitution assigned to maltose is identical with the current provisional formula which has found expression in recent text-books, and was proposed, along with alternative formulæ, by Fischer ("Untersuchungen über Kohlenhydrate und Fermente," 1884—1908, p. 92).

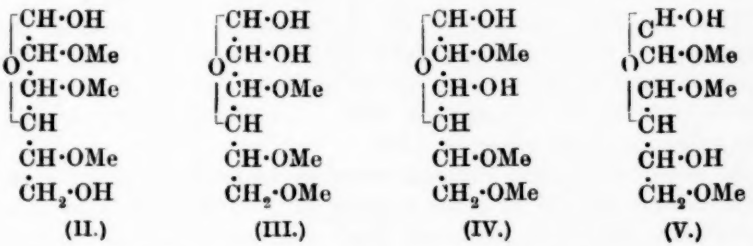
Following the general lines indicated in the previous research on lactose (*loc. cit.*), the methylation of maltose was effected by the agency of methyl sulphate and sodium hydroxide, and, as a precautionary measure designed to ensure that methylation was complete, the material isolated from this reaction was finally submitted to an alternative treatment with Purdie's reagent, namely, silver oxide and methyl iodide. Eight methyl groups were found to have been introduced into the maltose molecule, and heptamethyl methylmaltoside (VII), corresponding in the degree of substitution with the known octa-acetylmaltose, was isolated as a colourless gum, which distilled as a mobile syrup at 189—190°/0·09 mm. The compound was soluble in water and did not reduce Fehling's solution. It dissolved freely in methyl or ethyl alcohol or acetone, and showed $[\alpha]_D$ +89·6°, the equilibrium value for maltose itself being 137·7°.

There can be little doubt, in view of other results obtained in methylating reducing sugars with methyl sulphate, that this substance is chiefly the β-form, containing also the stereochemical α-modification.

When heptamethyl methylmaltoside was hydrolysed with 5 per cent. aqueous hydrochloric acid for three hours at 85—100°, a mixture of tetramethyl and trimethyl glucoses was obtained as the product of cleavage. This was a mobile syrup, and the separation of the two constituents was effected by careful fractionation in the high vacuum of the Gaede pump. Two pure fractions, collected at 131°/0·3 mm. and at 171°/0·23 mm., were isolated along with the transition fraction distilling at temperatures intermediate between these limits. From the transition fraction, as will be shown later, more of the pure fractions was isolated. The first fraction, distilling at the lower temperature, crystallised immediately on nucleation with a crystal of tetramethyl glucose (VIII), and its complete identity with the latter substance was proved by determination of the melting point and also of that of a mixture with an authentic specimen of tetramethyl glucose. The specific rotation of the specimen derived from the hydrolysis of the methylated methylmaltoside was in agreement with the accepted

equilibrium value, which is $[\alpha]_D + 83°$. We can therefore confirm the similar observation made by Purdie and Irvine (T., 1905, **87**, 1029), who also isolated this compound from the product obtained by methylating maltose with silver oxide and methyl iodide.

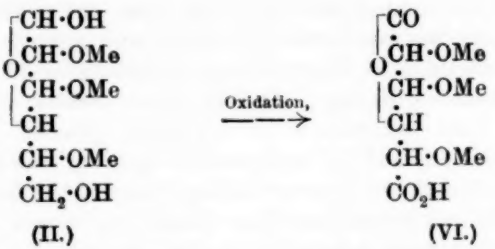
The identification of the substance distilling at 171°/0·23 mm. presented greater difficulty. The analytical results were in agreement with the formula of a trimethyl glucose. It reduced Fehling's solution, and its comparative stability towards permanganate indicated that it was a reducing sugar of the butylene oxide type. It did not crystallise after nucleation with a specimen of the trimethyl glucose isolated from the hydrolysis of heptamethyl methyl-lactoside (Haworth and Leitch, *loc. cit.*), and failed to give an osazone with phenylhydrazine. Of the four formulæ possible for a trimethyl glucose of the butylene oxide type, those numbered III and V may for these reasons be excluded from immediate consideration.



Moreover, it is clear from the presentation of these four possible formulæ that if proof could be found for the presence of a free primary alcohol group in the trimethyl glucose isolated during this investigation, this fact would definitely determine the constitution of the trimethyl hexose, as this terminal hydroxyl group is only present in formula II.

Accordingly, the trimethyl glucose was carefully oxidised with dilute nitric acid (D 1·2), and a liquid carboxylic acid was isolated which was shown also to be a lactone. On titration with *N*/10-alkali, an apparent neutral point was reached when rather less than one molecular proportion of alkali was introduced, and its behaviour on the subsequent addition of more alkali showed that a lactone ring was undergoing scission. Two molecular proportions of alkali were needed for complete neutralisation. The analytical data indicated that the lactonic acid had the molecular formula $C_9H_{14}O_7$, and contained three methoxyl groups. Its constitution can therefore only be represented by formula VI, and consequently the formula of the trimethyl glucose, from which by

oxidation the lactonic acid was obtained, is represented by formula II.



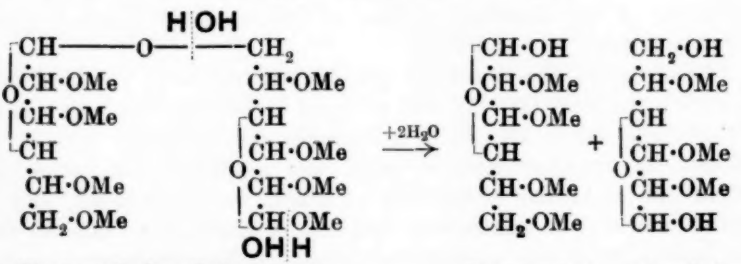
(II.) (VI.)

The product of oxidation is thus trimethyl saccharo-monolactone, and the primary alcohol group is shown to be present in the trimethyl glucose, since only such a group could undergo oxidation to a carboxyl group. This primary alcohol group has become exposed during the dissolution of partnership with the second methylated glucose residue occasioned by the hydrolysis of the biose.

The change in rotatory power, characteristic of lactones of the sugar series, was observed in the case of the lactonic acid. In aqueous solution, the value decreased from $[\alpha]_D$ +78° to +40° during four hours. In contact with a trace of hydrochloric acid, the value increased again to +56°.

A molecular weight determination in acetone solution by the ebullioscopic method gave the number 242, which is in fairly close agreement with that required (234) for the molecular formula $C_9H_{14}O_7$.

The behaviour of heptamethyl methylmaltoside (VII) on hydrolysis must therefore be formulated by the scheme outlined below, the dotted lines indicating the points of cleavage:

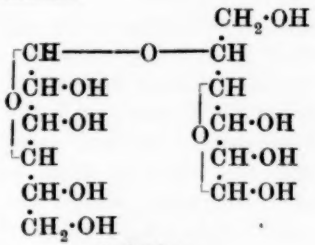


Heptamethyl methylmaltoside. Tetramethyl glucose. Trimethyl glucose.

(VII.) (VIII.) (II.)

Inasmuch as ordinary crystalline maltose is hydrolysed by contact with the enzyme maltase and not by emulsin, the disaccharide is to be regarded as glucose-α-glucoside, and since it exhibits an

upward mutarotation and belongs to the *d*-series, it may be described stereochemically as β-glucose-α-glucoside, and is structurally represented by formula I (p. 809). *iso*Maltose has probably the same structure, but is a glucose-β-glucoside. Maltose resembles melibiose in its behaviour (Bau, *Chem. Zeit*, 1897, **21**, 186), and so also cellobiose has properties in common with lactose (Hudson, *loc. cit.*). Definite structural formulæ have been assigned to one member in each of these pairs of disaccharides, namely, lactose and maltose, and it is legitimate, therefore, to assign a provisional structural formula to cellobiose (IX), especially in view of the fact that Denham and Woodhouse isolated from methylated cellulose on hydrolysis the same crystalline trimethyl glucose as the present authors obtained from methylated lactose (T., 1917, **111**, 244; 1918, **113**, 188). This cellobiose formula is of the same structural type as lactose:



Cellobiose.
(IX.)

Experiments are at present in progress to confirm this provisional constitution.

Experimental.

Methylation of Maltose with Methyl Sulphate: Preparation of Heptamethyl Methylmaltoside.

Maltose (30 grams) prepared by the action of barley diastase on potato starch was dissolved in the minimum volume of warm water. To the cooled solution methyl sulphate (28·5 c.c.) was added, and a 30 per cent. solution of sodium hydroxide (29 c.c.) was introduced very gradually with stirring. During the addition of the latter, the temperature was maintained at 35—40°, and the mixture kept overnight. The reducing action of the maltose towards Fehling's solution had then completely disappeared, and methylmaltoside had obviously been formed. The methylation of the remaining hydroxyl groups was effected at 70°, and the solution maintained faintly alkaline throughout. Methyl sulphate (85·5 c.c.) was added slowly at this temperature with efficient

mechanical stirring, and simultaneously 30 per cent. sodium hydroxide (82 c.c.) was introduced. It is important that the reagents should be added very gradually; a separate dropping funnel was kept for each reagent. The second part of the methylation, which has just been described, occupied one and a-half hours, after which the temperature was raised to 100° for half an hour. Extraction of the methylated maltoside with chloroform yielded, after drying over anhydrous magnesium sulphate and distillation of the solvent, 39 grams of a crude, straw-yellow syrup. This was subjected to another similar methylation at 70° with methyl sulphate, and, after careful removal of the whole of the chloroform used for the extraction, the residue weighed 28·2 grams.

By distillation in the high vacuum of the Gaede pump, 23 grams of a colourless syrup were collected at about 195°/0·28 mm. In order to ensure complete methylation of all the hydroxyl groups, this product was again methylated with alternative reagents, namely, with silver oxide and methyl iodide. The material was isolated in the usual way after this treatment, and yielded a colourless syrup distilling at 187°/0·06 mm. All the still residues were again methylated, and provided a further quantity of the required product. At this stage, the material from several preparations was combined and redistilled, when almost the whole distilled at 189—190°/0·09 mm., and showed n_D 1·4698. The compound was devoid of any reducing action on Fehling's solution, and behaved as a glucoside.

A methoxyl estimation indicated that complete methylation had taken place, eight methoxyl groups having been inserted in the maltose residue:

0·1290 gave 0·2493 CO_2 and 0·0957 H_2O. C = 52·7; H = 8·24.

0·0995 „ 0·4034 AgI. OMe = 53·52.

$C_{12}H_{14}O_3(OMe)_8$ requires C = 52·86; H = 8·37; OMe = 54·63 per cent.

The specific rotation of the heptamethyl methylmaltoside was determined in various solvents as follows:

Solvent.	c.	α_D.
Methyl alcohol	1·313	+89·5°
Ethyl alcohol	1·395	+89·6°
Acetone	1·173	+89·5°
Water	1·345	+81·4°

As the specific rotation in water appears slightly lower than was expected, an opportunity will be taken to confirm this value.

Hydrolysis of Heptamethyl Methylmaltoside.

Preliminary experiments indicated that the hydrolysis could best be effected with 5 per cent. aqueous hydrochloric acid solution at 85—100°. These conditions were also observed with the main bulk of the material, weighing 30 grams, which was dissolved in 400 c.c. of dilute acid of the above concentration. The solution was heated for one and a-half hours at 85°, and for a similar period at 100°. The mixture showed an initial rotation of α +12·9°, and the final reading was 9·8°. Further heating of a small sample of the solution produced no change in the rotation value. The procedure for the isolation of the products consisted in neutralisation with excess of barium carbonate, followed by filtration and evaporation of the filtrate under diminished pressure, when a syrup contaminated with barium chloride was obtained. The mineral matter was removed by extraction of the syrup with alcohol. After removal of this solvent, the residue was extracted with ether and the ethereal solution distilled. The syrup isolated in this way weighed 25 grams, and was carefully fractionated in a high vacuum.

Fraction I.—B. p. 120—131°/0·3 mm. Weight, 8·2 grams.
„ II.—B. p. 131—155°/0·23 mm. Weight, 8·4 grams.
„ III.—B. p. 171°/0·23 mm. Weight, 5·4 grams.

The first of these fractions crystallised immediately on nucleation with a specimen of tetramethyl glucose of the butylene oxide form. Fraction II was obviously a transition fraction which partly crystallised, and from it further quantities of the first and third fractions were ultimately obtained by repeated distillation. Fraction III had a boiling point which corresponded with that of a trimethyl hexose. All the fractions were colourless syrups which failed to give osazones and were not easily oxidised with permanganate. A recrystallisation of fraction I produced the easily recognisable needles of tetramethyl glucose, and its identity with this compound was shown by the rotatory power (see Purdie and Irvine, T., 1904, **85**, 1049), which was $[\alpha]_D$ +83° (equilibrium value) in water. Moreover, the melting point was correct for this substance, and a mixed melting-point determination showed no depression. The isolation of this substance from methylated maltose confirms the earlier observation recorded by Purdie and Irvine (T., 1905, **87**, 1029).

An analysis of fraction III, which showed n_D 1·4792, gave the following results:

0·1394 gave 0·2480 CO_2 and 0·1060 H_2O. C=48·52; H=8·02.
$C_9H_{18}O_6$ requires C=48·62; H=8·11 per cent.

An estimation of the methoxyl content characterised the substance as a trimethyl hexose:

0·1120 gave 0·3527 AgI. OMe=41·6.
$C_6H_9O_3(OMe)_3$ requires OMe=41·9 per cent.

The specific rotatory power of the trimethyl hexose was determined as follows:

Solvent.	c.	α_D.
Methyl alcohol.....	2·123	+67·8°
Acetone.....	2·151	+61·4°
Water	1·816	+69·3° → 71·0° (final value)

Oxidation.—With the object of determining the constitution of this hexose derivative, which clearly must represent one of the glucose residues of the maltose molecule, and therefore must be a trimethyl glucose, 3·5 grams of the substance were oxidised by gentle digestion with 40 c.c. of dilute nitric acid (D 1·2). To initiate the reaction, the temperature was maintained at 80° for a few minutes, and thereafter at 68° for three and a-half hours. Nitrous fumes had ceased to be evolved by this time, and the solution was almost colourless. The water was evaporated under diminished pressure at 35—40°; more water was repeatedly added during this procedure, and the solution again concentrated with the view of removing the whole of the nitric acid. Similar treatments with ethyl alcohol, followed by evaporation in a vacuum, served to eliminate the mineral acid, and the procedure was repeated with dry ether. Finally, a pale yellow syrup was obtained, which was dried and prepared for analysis by heating at 90° in a vacuum while passing through it a current of dry air. The weight of this oxidation product was 2·7 grams:

0·1094 gave 0·1847 CO_2 and 0·0618 H_2O. C=46·03; H=6·26.
0·0999 „ 0·2720 AgI. OMe=35·9.
$C_6H_5O_4(OMe)_3$ requires C=46·15; H=6·0; OMe=39·7 per cent.

From the above figures, the substance appeared to be a trimethyl saccharolactone, and this view was confirmed by titration with alkali.

0·0995 Gram was dissolved in dilute alcohol and rapidly titrated with *N*/10-sodium hydroxide, using phenolphthalein as indicator. When about 4·5 c.c. of the standard alkali had been added, the colour of the indicator remained for a few minutes and then disappeared. With each subsequent addition of alkali up to the amount of 9 c.c., the same phenomenon was observed. Excess of alkali was now introduced and the solution heated for

half an hour, and finally titrated to neutral point with standard acid. The amount of $N/10$-sodium hydroxide required for the complete neutralisation was 9·8 c.c., whereas a lactonic acid of the formula $C_9H_{14}O_7$ requires 9·7 c.c.

The specific rotation of trimethyl saccharolactone was determined in aqueous solution, and showed $[\alpha]_D$ 78°, falling to the value +40° after four hours. On catalysis with a trace of hydrochloric acid, the value again increased to +56°. A molecular weight determination in acetone solution by the ebullioscopic method gave the number 242, whilst the molecular weight required by the formula of the lactonic acid, $C_9H_{14}O_7$, is 234.

The authors are grateful to the Carnegie Trust for the grant of a Research Fellowship to one of them.

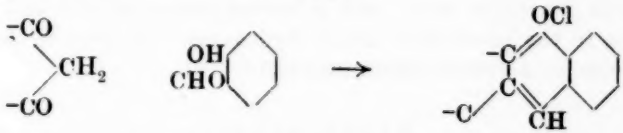
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

[*Received, June 2nd*, 1919.]

LXIV.—*Condensation of Deoxybenzoin and Aldehydes.*

By ANANDA KISORE DAS and BROJENDRA NATH GHOSH.

IT has been shown that aromatic *o*-hydroxy-aldehydes condense with substances containing ·CO·CH_2·CO· groups as in 1:3-diketohydrindene (Sastry and Ghosh, T., 1915, **107**, 1442), and in acetyl or benzoyl acetone (Chatterjee and Ghosh, T., 1918, **113**, 444) to form pyranol derivatives of the type

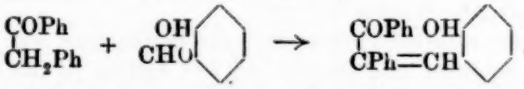


In order to extend this investigation, a substance of a similar type, namely, deoxybenzoin, was employed. In this case, instead of a ·CO·CH_2·CO· group, a ·CH_2· group is situated between one ·CO· group and the other phenyl group.

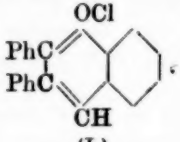
Several investigators have studied the interaction of benzaldehyde and deoxybenzoin, both acid and alkali being used as condensing agents (Japp and Klingemann, *Ber.*, 1888, **21**, 2935; Knoevenagel and Weissgerber, *Ber.*, 1893, **26**, 337; Stobbe and Niedenzu, *Ber.*, 1901, **34**, 3897; Klages and Tetzner, *Ber.*, 1902, **35**, 3971).

As our object was to synthesise pyranol derivatives, we began

with the condensation of salicylaldehyde and deoxybenzoin. It appeared that in the presence of alkali hydroxides, the condensation might proceed in the following way:



giving salicylidenedeoxybenzoin, which in the presence of hydrogen chloride might yield 2:3-diphenylbenzopyronium chloride (I).



(I.)

Accordingly, we conducted the reaction in the presence of alkali hydroxide, but found that no condensation took place under the conditions of the experiment. With hydrogen chloride, however, we obtained the desired compound. Decker and von Fellenberg (*Annalen*, 1909, **364**, 31) obtained the corresponding ferrichloride.

It was also found that no interaction took place between *p*-hydroxybenzaldehyde and deoxybenzoin in the presence of alkali hydroxide, but with hydrogen chloride the condensation product was formed; it could not, however, be obtained in a pure state.

Failing to obtain condensation products in the above two cases with alkali hydroxide, we extended the experiment to other aldehydes, such as anisaldehyde, piperonal, and *p*-tolualdehyde, using both alkali hydroxide and hydrogen chloride as condensing agents. In each case, a distinct condensation product was isolated. At present we are not in a position to offer an explanation of the apparent inactivity of *o*- and *p*-hydroxybenzaldehyde and deoxybenzoin in the presence of alkali hydroxide, but hope to deal with this point in a future communication.

Experimental.

Attempted Condensation of Salicylaldehyde and Deoxybenzoin in the Presence of Alkali Hydroxide.

1·2 Grams of salicylaldehyde and deoxybenzoin were dissolved in methyl alcohol, and to the mixture 3 grams of potassium hydroxide dissolved in 5 c.c. of water were added. The whole was then heated for two hours. A clear solution was obtained which, on the addition of water, gave a crystalline substance. This was collected, and the solution was acidified, but no solid substance separated.

2:3-*Diphenylbenzopyronium Chloride* (I).

A solution of 2 grams of deoxybenzoin and 1·2 grams of salicylaldehyde in methyl alcohol was saturated with dry hydrogen chloride. The colour of the solution changed from yellow to pink. It was kept overnight, but no precipitate separated. On the addition of very dilute hydrochloric acid, a dark red substance separated, which was dissolved in alcohol and reprecipitated by the addition of dilute hydrochloric acid, collected, washed with dilute hydrochloric acid, and kept in a vacuum over potassium hydroxide. On long keeping, it gradually became viscid. A portion of it, which was crystalline, was analysed:

0·1668 gave 0·4827 CO_2 and 0·0750 H_2O. C=78·9; H=5·0.

$C_{21}H_{15}OCl$ requires C=79·1; H=4·7 per cent.

The compound darkens at 85° and melts and decomposes at 176°.

Attempted Condensation of p-*Hydroxybenzaldehyde and Deoxybenzoin in the Presence of Alkali Hydroxide.*

A methyl-alcoholic solution of 1·2 grams of *p*-hydroxybenzaldehyde and 2 grams of deoxybenzoin was heated for about an hour with 3 grams of potassium hydroxide dissolved in 5 c.c. of water. A clear liquid was obtained, which was acidified as before, but nothing separated.

A condensation product was, however, obtained with hydrogen chloride as the condensing agent, but this compound could not be crystallised, and as it melted very indefinitely (170—185°), it appeared to be a mixture which could not be easily separated.

α-p-*Methoxybenzylidenedeoxybenzoin.*

A current of dry hydrogen chloride was passed through a methyl-alcoholic solution of molecular quantities of anisaldehyde and deoxybenzoin for a few minutes. After allowing the solution to remain for two days, a crystalline substance separated, which was collected and recrystallised from alcohol. It separated in colourless needles melting at 113°. (Found: C=83·77; H=5·8. $C_{22}H_{18}O_2$ requires C=84·09; H=5·70 per cent.)

p-*Methoxy-α-chlorobenzyldeoxybenzoin.*

This was prepared by supersaturating a methyl-alcoholic solution of molecular quantities of anisaldehyde and deoxybenzoin with

dry hydrogen chloride. The substance began to separate at once from the solution, and was collected next day. It was recrystallised from acetic acid, when it separated in colourless needles melting and decomposing at 152° (Klages and Tetzner give 144°). On testing the substance, it was found to contain chlorine. (Found: C = 75·50; H = 5·60. $C_{22}H_{19}O_2Cl$ requires C = 75·40; H = 5·40 per cent.)

It may be noted here that 3 : 4-methylenedioxy-α-chlorobenzyldeoxybenzoin and *p*-methyl-α-chlorobenzyldeoxybenzoin were similarly obtained.

3 : 4-*Methylenedioxybenzamarone*,

$$CH_2\langle\begin{matrix}O\\O\end{matrix}\rangle C_6H_3\cdot CH(CHPh\cdot COPh)_2.$$

This was prepared by heating a methyl-alcoholic solution of 4 grams of deoxybenzoin and 1·5 grams of piperonal with 3 grams of potassium hydroxide dissolved in 5 c.c. of water. The substance which separated was collected, washed, and crystallised from acetic acid, when colourless needles melting at 243—244° were obtained:

0·1347 gave 0·4031 CO_2 and 0·0673 H_2O. C = 82·38; H = 5·50.
$C_{36}H_{28}O_4$ requires C = 82·40; H = 5·30 per cent.

p-*Methylbenzamarone*, $C_6H_4Me\cdot CH(CHPh\cdot COPh)_2$.

This was prepared by boiling a methyl-alcoholic solution of 1·2 grams of *p*-tolualdehyde and 4 grams of deoxybenzoin with 3 grams of potassium hydroxide in 5 c.c. of water. The substance crystallised from acetic acid in colourless needles melting at 233—234°:

0·1103 gave 0·3461 CO_2 and 0·0676 H_2O. C = 85·50; H = 6·80.
$C_{36}H_{30}O_2,\frac{1}{2}H_2O$ requires C = 85·80; H = 6·30 per cent.

In conclusion, we beg to thank Principal F. W. Sudmersen for his keen interest in this work, and also the Chemical Society for a grant which has defrayed part of the expenditure.

THE CHEMICAL LABORATORY,
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[*Received, January 13th*, 1919.]

LXV.—*Condensation of Deoxybenzoin with Aromatic Aldehydes.*

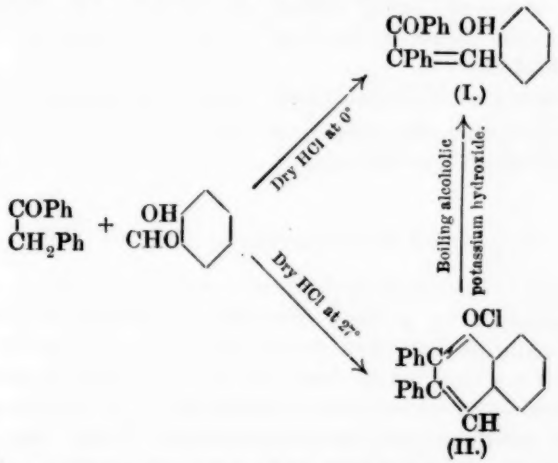
By Bawa Kartar Singh and Jatindra Kumar Mazumdar.

This work was undertaken with the object of extending the analogy which exists between deoxybenzoin and 1:3-diketones, inasmuch as both these substances may be condensed with aryl aldehydes by Knoevenagel's reaction. In the case of deoxybenzoin, it is the negative phenyl group that influences the reactivity of the hydrogen atoms of the methylene group, and thus acts similarly to one of the carbonyl groups in the 1:3-diketones:

$$\cdot CO\cdot CH_2\cdot CO\cdot + R\cdot CHO \longrightarrow \begin{matrix} CO\cdot C\cdot CO\cdot \\ \| \\ R\cdot CH \end{matrix}$$

$$C_6H_5\cdot CH_2\cdot CO\cdot C_6H_5 + R\cdot CHO \longrightarrow \begin{matrix} C_6H_5\cdot C\cdot CO\cdot C_6H_5 \\ \| \\ R\cdot CH \end{matrix}$$

With this object in view, several aryl aldehydes, namely, salicylaldehyde, *p*-hydroxybenzaldehyde, 2-naphthol-1-aldehyde, cinnamaldehyde, vanillin, *o*-aminobenzaldehyde, *p*-dimethylaminobenzaldehyde, piperonal, and *o*- and *p*-nitrobenzaldehyde* were condensed with deoxybenzoin through the agency of hydrogen chloride, alcoholic potassium hydroxide, and diethylamine.



* It was subsequently found that deoxybenzoin had already been condensed with piperonal, and *o*- and *p*-nitrobenzaldehyde by Stobbe and Wilson (*Annalen*, 1910, **374**, 237); these compounds are therefore omitted from this paper.

In the course of this work, it has been observed that different results are obtained by condensing deoxybenzoin and salicylaldehyde with hydrogen chloride at 0° and at 27°. At 0°, salicylidenedeoxybenzoin (I) is obtained, whilst at 27° pyranol formation takes place, as previously observed by Decker and von Fellenberg (*Annalen*, 1909, **364**, 1). These authors isolated the product in the form of the ferrichloride, but we isolated the hydrochloride (II) direct.

Experimental.

Salicylidenedeoxybenzoin (I).

0·8 Gram of salicylaldehyde was mixed with an alcoholic solution of 1 gram of deoxybenzoin. The mixture was cooled in ice and saturated with dry hydrogen chloride, when the colour of the solution changed to dark brown. The mixture was kept for two to three days, when an amorphous, brown precipitate formed, which was collected and crystallised twice from dilute alcohol. The substance darkens at 120° and melts at 160°. It is soluble in alcohol or acetic acid, but insoluble in water:

0·1850 gave 0·5686 CO_2 and 0·1042 H_2O. C = 83·6; H = 6·0.

$C_{21}H_{16}O_2$ requires C = 84·0; H = 5·40 per cent.

0·2 Gram of the substance was boiled under reflux with 10 c.c. of 50 per cent. alcoholic potassium hydroxide for two hours. The substance dissolved with change of colour. On cooling and acidifying with dilute hydrochloric acid, the original substance was precipitated.

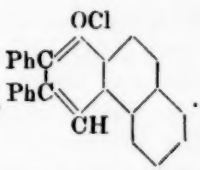
Condensation of salicylaldehyde with deoxybenzoin could not be effected through the agency of potassium hydroxide, although various methods were tried.

2:3-*Diphenylbenzopyronium Chloride* (II).

1·5 Grams of salicylaldehyde were mixed with 2 grams of deoxybenzoin dissolved in a small quantity of methyl alcohol. Dry hydrogen chloride was then passed through the mixture for two hours at 27°; a very bright deep red coloration was developed, and the solution acquired a syrupy consistency. On keeping for two days, red, needle-shaped crystals separated. They were collected and recrystallised from dilute acetic acid containing a little hydrochloric acid, when they formed red needles melting at 100°. The substance is soluble in alcohol or acetic acid, but insoluble in water:

0·1550 gave 0·4582 CO_2 and 0·0700 H_2O. C = 80·6; H = 5·0.
$C_{21}H_{15}OCl$ requires C = 79·1; H = 4·7 per cent.

0·5 Gram of the above pyranol compound was dissolved in alcohol and boiled under reflux with 20 c.c. of 10 per cent. alcoholic potassium hydroxide for three hours. The solution was then diluted with water and acidified with dilute acetic acid. The brown precipitate was collected, dissolved in alcohol, and again precipitated by water. It was identified as the compound (I), darkening at 120° and melting at 160°. (Found: C = 83·5; H = 6·0. $C_{21}H_{16}O_2$ requires C = 84·0; H = 5·4 per cent.)

2 : 3-*Diphenylnaphthapyronium Chloride*, 

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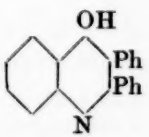
Two grams of deoxybenzoin and 1·6 grams of 2-naphthol-1-aldehyde were dissolved in methyl alcohol, and dry hydrogen chloride was passed into the solution for three hours at the ordinary temperature (25°). The solution gradually acquired a dark blue colour, and, after two to three days, dark blue needles separated. They were collected, washed with a little methyl alcohol, and recrystallised from dilute acetic acid, when they melted at 148—150°.

The compound is soluble in acetic acid, alcohol, or ether, but insoluble in water:

0·1255 gave 0·3738 CO_2 and 0·0566 H_2O. C = 81·16; H = 5·01.
$C_{25}H_{17}OCl$ requires C = 81·41; H = 4·61 per cent.

This substance decomposes gradually on keeping. It has been isolated in the form of the ferrichloride by Decker and von Fellenberg (*loc. cit.*).

4-*Hydroxy*-2 : 3-*diphenylquinoline*, 

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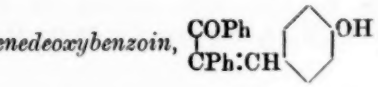
Two grams of deoxybenzoin and 1·6 grams of anthranilic acid were mixed together, powdered, and heated in an oil-bath at 130—150° for three days. The product was then rendered alkaline with dilute sodium hydroxide solution and extracted with ether. The aqueous portion was acidified with dilute acetic acid and again extracted with ether. A solid gradually separated from

the aqueous solution. This was collected, washed, and crystallised from alcohol, when colourless, rectangular cubes melting at above 300° were obtained. The compound is insoluble in water, soluble in acetic acid or ether, and sparingly so in aqueous sodium hydroxide or alcohol:

0·1357 gave 5·8 c.c. N_2 at 32° and 762 mm. N = 4·8.
$C_{21}H_{15}ON$ requires N = 4·53 per cent.

p-*Hydroxybenzylidenedeoxybenzoin*,  .

p-Hydroxybenzaldehyde and deoxybenzoin in molecular proportion were dissolved in a small quantity of ethyl alcohol, and the solution was cooled in ice and saturated with dry hydrogen chloride, when a change of colour took place at once. On allowing the mixture to remain for two to three days, a precipitate gradually formed, which was collected and crystallised from dilute acetic acid, separating in red needles melting at 155°. The substance is soluble in alcohol or acetic acid, but insoluble in water. It does not contain chlorine:

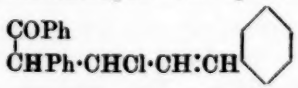
0·1460 gave 0·4465 CO_2 and 0·0722 H_2O. C = 83·4; H = 5·5.
$C_{21}H_{16}O_2$ requires C = 84·0; H = 5·4 per cent.

Vanillylidenedeoxybenzoin, .

Vanillin and deoxybenzoin in molecular proportion were condensed as above, when an oil was obtained which solidified in three to four days. This separated from hot alcohol as an amorphous, reddish mass melting at 146—148°. It is soluble in acetic acid, alcohol, or ether, but insoluble in water. It does not contain chlorine:

0·1274 gave 0·3755 CO_2 and 0·0596 H_2O. C = 80·4; H = 5·3.
$C_{22}H_{18}O_3$ requires C = 80·0; H = 5·4 per cent.

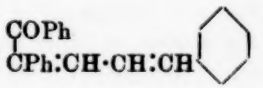
Cinnamylidenedeoxybenzoin hydrochloride,

 .

Deoxybenzoin and cinnamaldehyde in molecular proportion were condensed as above, and there was obtained a solid which separated from hot alcohol as an amorphous mass melting at 100°.

It is soluble in alcohol, acetic acid, or ether, but insoluble in water. The substance contains chlorine:

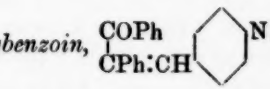
0·1238 gave 0·3609 CO_2 and 0·0657 H_2O. C = 79·5; H = 5·9.
$C_{23}H_{19}OCl$ requires C = 79·7; H = 5·5 per cent.

Cinnamylidenedeoxybenzoin,  .

Deoxybenzoin and cinnamaldehyde in molecular proportion were dissolved in a little alcohol, and the mixture was cooled in ice, a few drops of diethylamine being added. A crystalline precipitate formed within an hour, which separated from hot glacial acetic acid in snow-white needles melting at 145°. The yield was almost theoretical.

It is insoluble in water and sparingly soluble in ethyl alcohol or acetic acid:

0·1095 gave 0·3558 CO_2 and 0·0601 H_2O. C = 88·6; H = 6·1.
$C_{23}H_{18}O$ requires C = 89·0; H = 5·8 per cent.

p-*Dimethylaminobenzylidenedeoxybenzoin*,  .

p-Dimethylaminobenzaldehyde and deoxybenzoin in molecular proportion were condensed in the usual manner, and a solid was obtained which crystallised from dilute acetic acid in colourless needles melting at 98°. It is very readily soluble in ethyl alcohol or acetic acid, but insoluble in water:

0·1159 gave 4·6 c.c. N_2 at 28° and 761 mm. N = 4·6.
$C_{23}H_{21}ON$ requires N = 4·3 per cent.

This work was carried out at Dacca College in 1917.

THE CHEMICAL LABORATORY,
GOVERNMENT COLLEGE,
LAHORE, PUNJAB, INDIA. [*Received, February 6th*, 1919.]

LXVI.—*Trustworthiness of the Balance over Long Periods of Time.*

By George Dean.

During the prosecution of a series of atomic-weight determinations by the author, a paper was published on "The limitations of the balance" (Blount, T., 1917, **111**, 1035). The author there draws the conclusion, based on experiments with several balances, that although weighings of a given object made within a few hours —or even days—of each other may be concordant, this is not the case if they are extended over several months. A variation as high as 1·6 milligrams was detected, and attributed to the gradual shifting of the central knife edge.

If this conclusion is established, the accuracy of many atomic-weight determinations will be seriously impaired. The work referred to above is especially liable to this error, as a period of three to fifteen months intervened between the initial and final weighings. Fortunately, it was possible to test the magnitude of the error in this case. The experiments were carried out in weighed silica flasks, each provided with a similar silica flask as counterpoise. These were used in successive experiments, and, being appreciably affected by the chemical action, their weights, recorded during several years, were useless for the present purpose. One flask, however, being of inconvenient shape, had been used, re-weighed, and rejected. It was weighed after long intervals. The details of the weighings are as follows, the numbers representing the weights added to the counterpoise to make it balance the flask.

May 17th, 1917.	Flask treated with boiling nitric acid, washed with distilled water, dried, wiped, ignited, cooled in desiccator with counter, and both left on pans of balance before weighing	+0·001300 gram	
May 18th, 1917.	Merely replaced in balance and left all night before weighing	+0·001325 „	0·001312 gram.

The two were now left over calcium chloride under a bell glass for ten months.

Mar. 7th, 1918.	Replaced in balance, left all night and re-weighed	+0·001360 gram	
Mar. 8th, 1918.	Flask and counter, both carefully wiped and replaced, left all night on pans before weighing .	+0·001379 „	0·001374 gram.
Mar. 9th, 1918.	Merely replaced and left all night	+0·001382 „	

After a further interval of two months, a single weighing was taken:

July 23rd, 1918. Flask, etc., replaced in balance and left all night . . . . . 0·001415 gram.

The flasks were now left in the desiccator for ten months, the balance remaining practically unused:

May 20th, 1919.		Replaced in balance and left all night . . .	+0·001422 gram	
„ 23rd	„	Flask wiped and heated (but not counter), cooled in desiccator, in balance all night	+0·001419 „	
„ 26th	„	Both replaced in balance and left for week-end .	+0·001406 „	
„ 27th	„	Counterpoise, wiped, ignited, cooled in desiccator, both left in balance all night	+0·001474 „	0·001435 gram.
„ 28th	„	Both replaced in balance and left all night . .	+0·001480 „	
„ 31st	„	Both in desiccator 2 days, in balance 1 night . .	+0·001421 „	
June 3rd	„	Both in desiccator 2 days, in balance 1 night . .	+0·001425 „	

The total variation in weight of a flask weighing 40·65 grams, in two years, is thus +0·000123 gram, made up of +0·000062 gram in the first ten months, +0·000041 gram in the succeeding four months, and 0·000020 gram in the final ten months.

After carrying out determinations extending over several years, and depending on some thousands of elaborate weighings, it was satisfactory to find the error introduced by the duration of an experiment was so small as to be practically negligible. The fact that the variation was a steady increase rather favours the view that it is due to a displacement of the knife edge.

The test was more searching than if twin metal weights had been used; the flasks were more bulky; they were polished occasionally by breathing upon them and rubbing with a cloth, this being necessary in the atomic-weight experiments to remove a slight film deposited on the flask from the oven in which it was heated. As each flask had an external surface of about 250 sq. cm., there is a possibility of changes in weight from this treatment, as also from air condensation after heating.

The weighings were not made under ideal conditions. The room is small and has a low ceiling, with two doors and windows, is heated by a steam radiator, and subject to vibration from a ventilating fan. To minimise these drawbacks, the flasks were placed on the balance the night before the weighing, the windows

heavily curtained, and fan and radiator turned off. In this way, trustworthy readings were secured.

The method of swings was used, ten swings of the pointer to the left and nine to the right being recorded, and the point of equilibrium on the scale calculated. The rider was next shifted along the beam to increase the weight by 1 milligram, and the observations were repeated. Finally, the flasks and rider were removed from the balance, which was then left for at least an hour. It was then set swinging, and the true "zero" of the empty balance worked out. From the three equilibrium positions, the weight of the flask is easily calculated. It was necessary to adopt this tedious method, as the "zero" of the balance is rarely constant for more than a few hours at a time.

The balance was an ordinary short-beam instrument of (unknown) German make. It was in constant use except during the final ten months, when no weighings were made on it except those recorded above.

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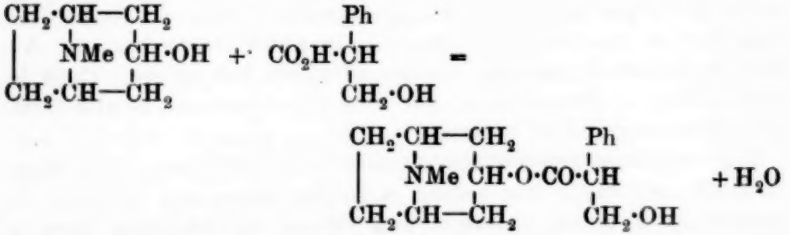
LXVII.—*The Isomeric Tropic Acids.*

By ALEX. McKENZIE and JOHN KERFOOT WOOD.

ALTHOUGH nearly forty years have elapsed since Ladenburg carried out his fundamental researches on the constitution of atropine, this alkaloid is still obtained exclusively from natural sources. This is undoubtedly due to the difficulties involved in the preparation in quantity of the two constituents of the atropine molecule, namely, tropine and *r*-tropic acid. The yield of atropine obtained by Ladenburg by the combination of the two constituents according to the equation



was apparently very small. Wolffenstein and Mamlock (*Ber.*, 1908, **41**, 723) have, however, shown that by acetylating tropic

acid, then converting into the acid chloride, and combining this with tropine, a good yield of acetylatropine hydrochloride can be obtained, and from the latter compound the acetyl group can be eliminated with the formation of atropine in a satisfactory yield. In the light of the experience of these authors, there should be no difficulty in effecting the synthesis of atropine in fair quantity provided that methods are available for the production of the requisite tropine and tropic acid.

The recent synthesis of tropinone by Robinson (T., 1917, **111**, 762) suggests the possibility of the production of synthetic tropine. Meanwhile, the present authors had been engaged in the examination of various methods for the preparation of tropic acid other than that from atropine itself, and the results are described in the present communication.

Ladenburg and Rügheimer (*Ber.*, 1880, **13**, 373; *Annalen*, 1883, **217**, 74) claim to have converted atropic acid into tropic acid in the following manner. Chlorotropic acid was first obtained by the direct addition of hypochlorous acid to atropic acid,

$$CH_2{:}CPh{\cdot}CO_2H + HClO = OH{\cdot}CH_2{\cdot}CClPh{\cdot}CO_2H,$$

and the chlorotropic acid was then reduced,

$$OH{\cdot}CH_2{\cdot}CClPh{\cdot}CO_2H + 2H = OH{\cdot}CH_2{\cdot}CHPh{\cdot}CO_2H + HCl.$$

It is apparent from Ladenburg's description that some difficulty was experienced by him in the reduction of the chlorotropic acid, although it is stated that the action proceeded smoothly when a mixture of zinc dust and iron filings was added to a solution of the acid in concentrated potassium hydroxide. It may be stated at once that our experience with this method was most disappointing. There was no difficulty in preparing the chloro-acid, but all our attempts to reduce it to tropic acid, whether by Ladenburg's method or in other ways, ended in failure. In many of these experiments the chloro-acid was partly recovered, whilst in one or two cases the product was free from halogen and possessed the melting point of atroglyceric acid. In view of the difficulties encountered, we drew the conclusion that this method is not a practical one for the preparation of appreciable quantities of tropic acid.

Spiegel (*Ber.*, 1881, **14**, 235) obtained tropic acid by heating acetophenonecyanohydrin with hydrochloric acid at 130°, and then acting on the resulting β-chlorohydratropic acid with a solution of sodium carbonate at 120°. There are no details quoted in the paper regarding the yield of tropic acid.

A method which we employed was the reduction of the formylphenylacetic ester, prepared by Wislicenus's method, from ethyl formate and ethyl phenylacetate. This ester was reduced in

ethereal solution by means of aluminium amalgam, and the resulting tropic ester was hydrolysed:

$$CH_2Ph\cdot CO_2Et \longrightarrow CHO\cdot CHPh\cdot CO_2Et \longrightarrow OH\cdot CH_2\cdot CHPh\cdot CO_2Et \longrightarrow OH\cdot CH_2\cdot CHPh\cdot CO_2H.$$

After these experiments were completed by us, the method was described by Müller (*Ber.*, 1918, **51**, 252; D.R.-P. 302737), and also by Wislicenus and Bilhuber (*Ber.*, 1918, **51**, 1237), the latter chemists having used methyl formylphenylacetate. Müller states that the aluminium residue retains almost half of the formyl ester, which is therefore not reduced, and, according to him, cannot be removed from the residue by means of ether. Wislicenus and Bilhuber also noticed that a portion of the formyl ester was retained by the aluminium. We also obtained a small yield of tropic acid by this process.

Of the methods we have studied for the preparation of tropic acid, the following gave by far the best result. Acetophenone was converted into atrolactinic acid, which, on being heated under diminished pressure, gave atropic acid; this in turn was converted into β-chlorohydratropic acid by the action of hydrogen chloride on its ethereal solution, and the halogen was then displaced by boiling the acid with an aqueous solution of sodium carbonate:

$$\begin{matrix}Ph\\Me\end{matrix}\!\!>\!CO \longrightarrow \begin{matrix}Ph\\Me\end{matrix}\!\!>\!C\!<\!\begin{matrix}OH\\CN\end{matrix} \longrightarrow \begin{matrix}Ph\\Me\end{matrix}\!\!>\!C\!<\!\begin{matrix}OH\\CO_2H\end{matrix} \longrightarrow$$

$$\begin{matrix}Ph\\H_2C\end{matrix}\!\!>\!C\cdot CO_2H \longrightarrow \begin{matrix}Ph\\ClH_2C\end{matrix}\!\!>\!C\!<\!\begin{matrix}H\\CO_2H\end{matrix} \longrightarrow \begin{matrix}Ph\\OH\cdot CH_2\end{matrix}\!\!>\!C\!<\!\begin{matrix}H\\CO_2H\end{matrix}.$$

The resolution of *r*-tropic acid into its optically active components is described by Ladenburg and Hundt (*Ber.*, 1889, **22**, 2591). The acid was dissolved in dilute aqueous alcohol and neutralised by quinine. The resulting salt was crystallised until the melting point was constant, the value 186—187° being given. The tropic acid obtained from this salt melted at 127—128°, and gave $[\alpha]_D$ +71·4° "als Mittel aus Versuchen in verschieden concentrirten Lösungen." This value for the specific rotatory power of the *d*-acid has no significance, since the solvent employed is not quoted.

Amenomiya (*Arch. Pharm.*, 1902, **240**, 498) acted on a mixture of 10 grams of atropine and *l*-hyoscyamine with water, and obtained a mixture of *r*-tropic acid and a small quantity of the *l*-isomeride. This was neutralised with quinine, and the resolution conducted according to Ladenburg and Hundt. The quinine *d*-salt melted at 189—190°. The resulting acid was washed with benzene to free it from atropic acid; it then melted at 126—127°, whilst the value

$[\alpha]_D^{20}$ +71·3° for $c=2·384$ in ethyl-alcoholic solution is quoted. From the mother liquors of the quinine salt, a lævorotatory tropic acid melting at 126° and giving $[\alpha]_D^{20}$ −72·75° in aqueous solution was prepared. No analyses of the optically active acids are quoted either by Ladenburg and Hundt or by Amenomiya. Moreover, the quantity of inactive acid at the disposal of those investigators would seem to have been rather inadequate for the purpose they had in view.

Atropine is the *dl*-tropyl ester of tropine, whilst *l*-hyoscyamine is the *l*-tropyl ester of tropine. Hyoscyamine has the grouping ·CO·CH·, and, in accordance with the work carried out by one of us and his co-workers on racemisation with alcoholic alkali, it might be expected that this alkaloid would undergo racemisation with alcoholic alkali. Data in the literature show that this is the case, but the point is perhaps worthy of further investigation. Pure atropine is optically inactive, but the atropine of commerce is often slightly lævorotatory, owing to its containing some hyoscyamine. In all probability, the plant builds up the pure *l*-hyoscyamine, and this is racemised either in the plant itself or during the commercial preparation of atropine. The question (which probably has received attention from the manufacturers of atropine) suggests itself: Would it be possible to isolate pure hyoscyamine from the plant, or would this compound racemise so readily that its isolation on the large scale would be impossible? One of the sources of atropine is *Hyoscyamus muticus*—which is said to contain hyoscyamine only. Now it is significant that alkali always appears to be used in the extraction of atropine from plants. It might be possible technically to avoid the use of alkali in the extraction, and thus obtain a salt of pure hyoscyamine. If this were practical, the advantage would be very great, since *l*-hyoscyamine in its mydriatic power is reported as being one hundred times as active as its *d*-isomeride. It would therefore be a much better mydriatic than atropine. Similar considerations apply to pilocarpine. It has, however, to be recognised that it is doubtful if the naturally occurring *l*-hyoscyamine or its *d*-isomeride has ever been prepared in a state of purity, and it seems very probable that Barrowcliff and Tutin (T., 1909, **95**, 1966) are correct when they suggest that the interesting physiological results of Cushny on the comparison of the *d*- and *l*-hyoscyamines were obtained with alkaloids which were not optically pure.

By the hydrolysis of *l*-hyoscyamine, Gadamer (*Arch. Pharm.*, 1901, **239**, 294) obtained a lævorotatory tropic acid melting at 123—124° and having $[\alpha]_D^{20}$ −69·49° in aqueous solution. A purer specimen was obtained by heating an aqueous solution of *l*-hyoscine;

the resulting acid was washed with benzene to free it from the small amount of atropic acid present, and the residue then crystallised from water. The resulting tropic acid melted at 125—126° and gave $[\alpha]_D$ −71·81° in aqueous solution.

As it appeared to the present authors to be of some importance to establish the purity of the *d*- and *l*-tropic acids, the resolution of the *r*-acid was carried out as described in the experimental portion of this paper. The *d*-acid was obtained by means of quinine, the solvent used being ethyl alcohol. It melted at 128—129° and had $[\alpha]_D^{16}$ +72·2° for $c=2·695$ in ethyl-alcoholic solution, a result which is nearly identical with that of Amenomiya, who found $[\alpha]_D$ +71·3°. We obtained the *l*-acid by means of morphine, the solvent being ethyl alcohol. This acid melted at 128—129°, and had $[\alpha]_D^{13}$ −72·5° for $c=2·578$ in ethyl-alcoholic solution and $[\alpha]_D^{15}$ −79·0° for $c=1·538$ in aqueous solution. The lævorotatory acid of Amenomiya, which gave $[\alpha]_D$ −72·75° in aqueous solution, and Gadamer's acid, with $[\alpha]_D$ −69·49° in aqueous solution, were therefore not optically pure.

The results described in the present paper were practically completed towards the end of 1917, but publication has been delayed owing to the pressure of other work. Since the present paper was written, King (this vol., p. 476) has described the resolution of tropic acid, and our values for the specific rotatory powers of the optically active acids are in close agreement with those given by him. It is therefore satisfactory that the constants for these important acids have at last been definitely settled.

Experimental.

Reduction of Ethyl Formylphenylacetate.

As the reduction of this ester has already been described in the literature, it is unnecessary to describe our experience of the method. The ester used was the liquid modification, which was prepared by the action of sodium on a mixture of ethyl phenylacetate and ethyl formate, and purified through the copper derivative, as described by Wislicenus. In the bulk of the experiments, the reducing agent employed was aluminium amalgam. The ester was also reduced by the action of sodium on a solution of the ester in glacial acetic acid. The yields of the pure recrystallised tropic acid varied from 16 to 30 per cent. of the theoretical, calculating from the phenylformylacetic ester used.

Preparation of Atrolactinic Acid.

This acid was prepared as described by McKenzie and Clough (T., 1912, **101**, 393). The following details of a typical preparation may be given.

To a mixture of 80 grams of potassium cyanide (98 per cent.), 100 grams of acetophenone, and 5 c.c. of water, fuming hydrochloric acid (D 1·2) was added from a dropping funnel at the rate of twelve to fifteen drops at a time, the mixture being shaken vigorously after each addition. This operation lasted for five hours, 15 c.c. of acid being added in each of the first two hours and 20 c.c. in each of the subsequent hours. During the first three hours, the mixture was maintained at the ordinary temperature, so that the acetophenone did not solidify, but towards the close it was cooled in ice-cold water. When the addition of the acid was complete, the mixture was allowed to remain for half an hour, and the oil then poured off and washed with water. A further small quantity of oil was obtained by adding water to the sludge left in the reaction flask. The oil was then poured into 200 c.c. of hydrochloric acid (D 1·2) and left overnight. Sodium hydroxide solution was added until the solution was neutral, and then three times the theoretical amount of the same alkali (calculated on the acetophenone used) was added, and the mixture distilled in a current of steam until the evolution of ammonia ceased. About 65 grams of acetophenone were recovered. The contents of the distillation flask were evaporated until the separation of solid started. On cooling, the crystals were separated and acidified with hydrochloric acid, using Congo-red as indicator. The atrolactinic acid was filtered off, the filtrate evaporated further, and cooled; the resulting crystals contained some sodium chloride, from which the acid was separated by means of ether. Some additional acid was obtained from the filtrates. The ethereal solution of the acid was dried with anhydrous magnesium sulphate, the ether expelled, and the atrolactinic acid crystallised from water. The yield was 35 grams of crystallised acid, and this corresponds with a yield of 73 per cent. on the acetophenone converted.

Professor Kipping kindly suggested to us a modification of this method which gives good results. After the cyanohydrin was hydrolysed, water was added, and the acetophenone removed by distillation in steam. The hot acid solution was then filtered and cooled, when atrolactinic acid separated. A further quantity can be obtained by extracting the filtrate with ether. In employing this method, it should, however, be borne in mind that sufficient water must be added after the hydrolysis of the cyanohydrin, and

that the subsequent heating in the presence of hydrochloric acid should not be unduly prolonged, otherwise the atrolactinic acid may be partly converted into atropic acid. Ladenburg and Rügheimer (*loc. cit.*) have pointed out that when atrolactinic acid is boiled under a reflux condenser with moderately dilute hydrochloric acid for some time, then diluted with water, and distilled, small quantities of atropic acid pass over with the steam. With more concentrated hydrochloric acid, appreciable quantities of *iso*atropic acid are formed.

Preparation of Atropic Acid.

The process of Ladenburg and Rügheimer, to which reference has just been made, is not a convenient one for the preparation of atropic acid in quantity. Moreover, the method described by Kraut (*Annalen*, 1863, **128**, 282; compare also Fittig and Wurster, *Annalen*, 1879, **195**, 147), whereby atropine is boiled with barium hydroxide, is not very practical when the expense of atropine is considered, and the same criticism may be passed on Lossen's method of heating atropine with fuming hydrochloric acid at 120—130° (*Annalen*, 1866, **138**, 132).

We found that atrolactinic acid can be converted into atropic acid by distillation under diminished pressure. Atrolactinic acid contains water of crystallisation, but it is not necessary to dehydrate the acid before submitting it to distillation. The method is a convenient one, but certain precautions require to be taken in order to secure a good yield. The chief difficulty arose from the ease with which atropic acid is transformed under the agency of heat into α- and β-*iso*atropic acids (Fittig and Wurster, *loc. cit.*). We carried out the distillation in a silica flask with a capacity of 110 c.c. and provided with a side-tube of 12 mm. internal diameter and 28 cm. in length. The side-tube acts as a suitable condenser, and there is no danger of it becoming choked owing to the solidification of the condensed atropic acid, as is the case when an ordinary distilling flask is used. Experience showed that it is very advisable to heat the atrolactinic acid with a free flame rather than to use an oil-bath. If the distillation is carried out too slowly, a viscous residue of the *iso*atropic acids is left in the distilling flask, and the yield of atropic acid is poor. On the other hand, if the operation is conducted too rapidly, some atrolactinic acid passes over along with the atropic acid; the two acids are, however, easily separated by taking advantage of their very different solubilities in water, atropic acid dissolving, according to Kraut, in 692·5 parts of water at 19·1°, whilst the solubility of

atrolactinic acid was found by Lennart Smith (*J. pr. Chem.*, 1911, [ii], **84**, 737) to be 17·04 parts per litre of water at 18°. Under a pressure of 10—15 mm., an oil distils at 177—179° and solidifies quickly. The distillate is dissolved in a warm mixture of ethyl alcohol and water, and hot water is then added until the liquid becomes cloudy. The atropic acid separates on cooling in the form of iridescent leaflets. Should the melting point of the dried crystals indicate that the atropic acid is not quite pure, the crystals are left for some time in contact with water in order to remove atrolactinic acid.

The results of three experiments may be given:

(1) Nineteen grams of dehydrated atrolactinic acid gave 12 grams of atropic acid.

(2) Twenty grams of dehydrated atrolactinic acid gave 13 grams of atropic acid.

(3) Twenty-one grams of dehydrated atrolactinic acid gave 13·5 grams of atropic acid.

The time of distillation was fifteen minutes. The mean yield from the above figures is 72 per cent. of the theoretical; a further small quantity of atropic acid may be obtained from the mother liquors.

The acid melts at 106—107°. It gave C = 73·0; H = 5·5. (Calc.: C = 73·0; H = 5·4 per cent.)

This is a much more practical method for preparing atropic acid than that described by Ladenburg and Rügheimer (*Ber.*, 1880, **13**, 2041), who also used acetophenone as the starting point. They formed acetophenone dichloride, $CMePhCl_2$, which, by means of potassium cyanide and ethyl alcohol, was converted into the nitrile, $CMePh(CN)\cdot OEt$, and this, on hydrolysis by baryta, gave the barium salt of ethyl atrolactinic acid, $CMePh(CO_2H)\cdot OEt$. Atropic acid was obtained from the latter acid by treatment with concentrated hydrochloric acid. The method now described is also more practical than Spiegel's method, whereby atropic acid is produced by boiling β-chlorohydratropic acid with aqueous sodium hydroxide.

Preparation of β-Chlorohydratropic Acid.

An interesting study of the additive compounds of atropic acid and the halogen acids is described by Merling, who obtained β-chlorohydratropic acid by heating atropic acid with fuming hydrochloric acid in a sealed tube at 100° for five hours (*Annalen*, 1881, **209**, 1). The yield of the chloro-acid is not stated, but it is certain that the method is not a practical one, as atropic acid

would, under the experimental conditions, undergo considerable transformation into the *iso*atropic acids, and the formation of these acids is indicated in Merling's description.

The following is a convenient method for preparing β-chlorohydratropic acid. Ten grams of atropic acid were dissolved in 200 c.c. of dry ether free from alcohol, and a current of dry hydrogen chloride was passed in slowly for about two hours. The solution was kept warm during this period, the flask containing it having been attached to a reflux condenser provided with a calcium chloride drying tube. The solution was then kept overnight, and the hydrogen chloride again passed through the warm solution next day for four to five hours. After the bulk of the ether was removed by distillation, the residual liquid was allowed to evaporate spontaneously. An almost completely solid residue was obtained which, after two crystallisations from carbon disulphide, was sufficiently pure for analysis. Only one crystallisation is necessary when the chloro-acid is to be used for conversion into tropic acid. The acid melted at 88—89°, whereas Merling gives 87—88°. (Found: Cl = 19·3. Calc.: Cl = 19·2 per cent.)

Ten grams of atropic acid gave 10 grams of the chloro-acid, a yield of 80 per cent. of the theoretical.

Conversion of β-Chlorohydratropic Acid into Tropic Acid.

Merling (*loc. cit.*) found that the chloro-acid could be hydrolysed by heating with a solution of potassium carbonate. The present authors have examined the hydrolysis under various conditions with the object of securing as good a yield of tropic acid as possible, since certain secondary reactions are liable to occur. Those reactions are (*a*) the tendency for the formation of styrene through the elimination of hydrogen chloride and carbon dioxide, as observed by Merling, and (*b*) the readiness with which tropic acid in the presence of alkalis loses water and passes into atropic acid (Hesse, *J. pr. Chem.*, 1901, [ii], **64**, 286). The action of water alone was found to be unsatisfactory, but better results were obtained with aqueous sodium carbonate. The amount of sodium carbonate used was rather less than would be required to neutralise the original acid and the hydrochloric acid formed during the hydrolysis; there was practically no difference in the yield whether all the sodium carbonate was added at the beginning or gradually during the time of boiling. As an example, the following experiment may be quoted.

Four grams of the chloro-acid were mixed with 80 c.c. of water, and the mixture was boiled under a reflux condenser. A solution

of sodium carbonate (1·73*N*) was run in slowly, the boiling being maintained; 24·1 c.c. were added in the course of fifteen minutes, the boiling being then continued for a further three and a-half hours without the addition of any further quantity of alkali. On cooling, the solution was faintly alkaline; it was extracted with ether to remove styrene, acidified with dilute sulphuric acid, and extracted five times with ether. The ethereal solution was dried with sodium sulphate, and to the oily residue which remained after the removal of the ether, benzene was added. The resulting crystals were separated, washed with benzene, and dried. The yield was 2·32 grams and the melting point 116—117°. The aqueous solution which had been extracted with ether gave an additional 0·2 gram of tropic acid when extracted for five hours in a continuous extractor. Yield=70 per cent. Equivalent: Found: 166·6. Calc.: 166·1.

The residue obtained by the evaporation of the benzene filtrates reduced alkaline permanganate strongly, and doubtless consisted of a mixture of atropic and tropic acids.

In a similar experiment, using 10 grams of the chloro-acid, the yield of tropic acid amounted to 61 per cent. of the theoretical.

The tropic acid obtained in this manner was free from atropic acid.

The yield was smaller when sodium hydroxide was used in place of sodium carbonate. Solutions of sodium acetate and silver nitrate were also employed as hydrolysing agents, but in neither case was the yield of tropic acid so good as when sodium carbonate was used.

Attempts were made to study the hydrolysis from the kinetic point of view, but for various reasons these proved unsuccessful. At the boiling point, the reaction takes place too rapidly to permit of accurate determinations of the velocity of reaction, whilst at lower temperatures the solubility of the acid in water is too small. An attempt was made to overcome the latter difficulty by using a mixture of alcohol and water as the solvent, but under these conditions the velocity of reaction was reduced to such small dimensions as to be impossible of accurate determination.

Attempts to Reduce Chlorotropic Acid.

The method described by Ladenburg and Rügheimer for the preparation of chlorotropic acid was followed. The chlorotropic acid obtained melted at 129—130°, in agreement with the value given by Ladenburg, namely, 128—130°.

Reference has already been made in the theoretical portion of

the paper to the failure which attended our numerous efforts to reduce chlorotropic acid to tropic acid. Ladenburg describes the action as taking place when zinc dust and iron filings are added to a solution of the acid in a concentrated aqueous solution of potassium hydroxide, but no information is given regarding the actual concentration of the alkali he used. We made numerous experiments, using alkaline solutions of different concentrations. When the chlorotropic acid was dissolved in a solution of sodium or potassium hydroxide containing 20 grams of alkali in 100 c.c. of water and left for several days in contact with zinc dust and iron filings, the product which was obtained after the removal of the dissolved zinc and the extraction of the acidified portion by means of ether was a substance of indefinite melting point, and still contained chlorine. With a more concentrated solution of alkali (10 grams of potassium hydroxide in 10 grams of water), the product was free from chlorine. It appeared to be a mixture, as it had a strong reducing action on alkaline permanganate, but on treatment with benzene, part of it was sparingly soluble, and this, after washing with benzene, was practically devoid of reducing action. It was soluble in water, melted at 144—146°, and was probably atroglyceric acid, which melts, according to Fittig and Kast (*Annalen*, 1881, **206**, 32), at 146°.

Other reducing agents which were tried were sodium amalgam, zinc and hydrochloric acid, sodium hydroxide and aluminium powder, and aluminium amalgam. In each case, chlorotropic acid was recovered.

Preparation of the Optically Active Tropic Acids.

85·4 Grams of hydrated quinine (1 mol.) were dissolved in 850 c.c. of absolute ethyl alcohol at 17°, and 37·5 grams of *r*-tropic acid (1 mol.) were added with stirring until the solution was homogeneous. Crystallisation began after five minutes, and proceeded rapidly. After nineteen hours at the ordinary temperature, the crystals were separated; after remaining on a porous plate for three days, they amounted to 71 grams. Crystallisation was carried out another eight times from ethyl alcohol. The alcohol was distilled off from the filtrate from each successive crystallisation, the residue decomposed by dilute sulphuric acid, and the tropic acid extracted with ether and dried with sodium sulphate. The progress of the resolution was indicated by determining the specific rotatory power of the successive acids in ethyl-alcoholic solution, the following values for $[\alpha]_D$ being obtained: $-54{\cdot}2°$, $-36{\cdot}7°$, $-6{\cdot}1°$, $+23{\cdot}1°$, $+41{\cdot}2°$, $+60{\cdot}8°$, $+67{\cdot}1°$, $+69{\cdot}4°$,

$+69{\cdot}6°$. The quinine *d*-salt amounted to 25·5 grams; it separated from ethyl alcohol in felted leaflets grouped in rosettes melting at 190—191°; 100 c.c. of its ethyl-alcoholic solution contain about 0·55 gram of the salt at 13°. The salt was decomposed by dilute sulphuric acid, and the tropic acid repeatedly extracted with ether, 7·2 grams of pure *d*-acid being obtained.

d-*Tropic acid* is sparingly soluble in benzene, from which it separates in lustrous needles melting at 128—129°. It crystallises from water in glassy needles and plates grouped in rosettes:

0·1858 gave 0·4421 CO_2 and 0·1043 H_2O. C = 64·9; H = 6·3.

$C_9H_{10}O_3$ requires C = 65·0; H = 6·1 per cent.

Its specific rotation was determined in the following solvents:

(*a*) Ethyl alcohol:

$$c = 2{\cdot}695,\ l = 2;\ \alpha_D^{16} + 3{\cdot}89°;\ [\alpha]_D^{16} + 72{\cdot}2°.$$

(*b*) Water:

$$c = 1{\cdot}515,\ l = 2;\ \alpha_D^{16} + 2{\cdot}43°;\ [\alpha]_D^{16} + 80{\cdot}2°.$$

(*c*) Acetone:

$$c = 2{\cdot}19,\ \ l = 2;\ \alpha_D^{13} + 3{\cdot}67°;\ [\alpha]_D^{13} + 83{\cdot}8°.$$

For the preparation of the *l*-isomeride, 9 grams of acid with $[\alpha]_D - 54{\cdot}2°$ for $c = 2{\cdot}65$ in ethyl-alcoholic solution, and 4 grams of acid with $[\alpha]_D - 36{\cdot}7°$ for $c = 2{\cdot}574$ in ethyl-alcoholic solution (obtained from the first two filtrates in the resolution just described), were united and added to a warm solution of 23·8 grams of morphine in 350 c.c. of ethyl alcohol. On cooling, glassy crystals began to separate, and these were collected on the following day. The product, dried in air at the ordinary temperature, amounted to 32·5 grams. It was crystallised from ethyl alcohol six times. The tropic acid recovered from the mother liquors from these crystallisations gave the following values for $[\alpha]_D$ in ethyl-alcoholic solution: $-13{\cdot}5°$, $-28°$, $-56°$, $-59{\cdot}4°$, $-60{\cdot}7°$, $-63°$. Although the morphine salt (14 grams) was not yet quite pure, it was deemed advisable at this stage to decompose it with dilute sulphuric acid. The resulting acid (4 grams) was nearly pure, giving the value $[\alpha]_D - 71{\cdot}3°$ in ethyl-alcoholic solution. The pure acid was obtained after one crystallisation from water.

l-*Tropic acid* melts at 128—129°. Equivalent: Found: 166·5. Calc.: 166·1. The values for its rotatory power were determined in the following solvents, and are in agreement with the corresponding values for its *d*-isomeride:

(*a*) Ethyl alcohol:

$$c = 2{\cdot}578,\ l = 2;\ \alpha_D^{13} - 3{\cdot}74°;\ [\alpha]_D^{13} - 72{\cdot}5°.$$

(*b*) Water:

$$c = 1{\cdot}538,\ l = 2;\ \alpha_D^{15}\ -2{\cdot}43°;\ [\alpha]_D^{15}\ -79{\cdot}0°.$$

(*c*) Acetone:

$$c = 1{\cdot}806,\ l = 2;\ \alpha_D^{15}\ -3{\cdot}01°;\ [\alpha]_D^{15}\ -83{\cdot}3°.$$

The authors desire to acknowledge the able assistance rendered by the late Mr. Harold Halcro Johnston, B.Sc., in the earlier stages of this research. They are also indebted to Professors G. G. Henderson and F. S. Kipping for a supply of atrolactinic acid.

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UNIVERSITY OF ST ANDREWS. [*Received, June 4th*, 1919.]

LXVIII.—*The Absorption Spectra of the Nitric Esters of Glycerol.*

By HARRY HEPWORTH.

IN 1906, Kast (*Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1906, **1**, 225) discovered that nitroglycerin or glyceryl trinitrate is capable of existing in two isomeric forms in the solid state, a labile isomeride melting at 2·8° and a stable form melting at 13·5°. In a later paper on this subject by Nauckhoff (*ibid.*, 1911, **6**, 124), in which a description of the crystalline structure of the isomeride of higher melting point is given, the author differs from Kast in being unable to isolate the isomeride of lower melting point. The question of the existence of a second solid form of nitroglycerin has been carefully investigated by Hibbert ("Eighth International Congress of Applied Chemistry," 1912, **4**, 37), who has not only confirmed the existence of two solid isomerides, but has also investigated the various conditions under which each may be obtained.

Hibbert has compared these two solid isomerides with the two isomeric forms of benzophenone, and although he justly points out that structural isomerism is theoretically possible, yet on the whole the evidence points to the two forms of nitroglycerin being physical isomerides one of the other. This conclusion is largely based on the views of Schaum (*Annalen*, 1898, **300**, 209), according to whom the criterion between chemical and physical isomerism is to be found in the fact that with purely physical isomerides, inoculation of the solid labile with the solid stable form brings about the complete conversion of the former in the absence of any solvent.

Now it is evident that if the two solid forms of nitroglycerin are to be represented by two different structural formulæ, then the labile and stable forms should give rise to two different chemical compounds, either in the liquid state or in solution, and it is reasonable to suppose that these solutions will exhibit different absorption spectra. Aqueous solutions of nitroglycerin derived from the two forms have been examined spectrographically, and found to give identical spectra (Fig. 1), from which it is clear that there is no evidence of chemical isomerism in solution, and that the labile and solid forms of nitroglycerin are to be regarded as physical isomerides. Since the nitroglycerins examined showed general absorption only, it is improbable that an equilibrium mixture of dynamic isomerides is obtained when either form is dissolved in water.

The absorption spectrum of a sample of commercial nitroglycerin has also been determined as a matter of interest. It will be observed (Fig. 1) that the latter is much more absorptive than pure nitroglycerin. This cannot be due to the presence of lower nitrates, as the latter are soluble in water.

The lower nitrates of glycerol have been investigated by Will (*Ber.*, 1908, **41**, 1107), and the glyceryl $\alpha\beta$- and $\alpha\gamma$-dinitrates were prepared and separated as described by him. It is evident that in the case of the dinitrates, the two isomerides may have the structural formulæ

$$\begin{array}{l} CH_2\cdot OH \\ CH\cdot O\cdot NO_2 \\ CH_2\cdot O\cdot NO_2 \end{array} \quad \text{and} \quad \begin{array}{l} CH_2\cdot O\cdot NO_2 \\ CH\cdot OH \\ CH_2\cdot O\cdot NO_2 \end{array}$$

and should therefore give rise to two different absorption spectra. The absorption in aqueous solution was investigated, with the results shown in Fig. 2. It will be observed that the $\alpha\beta$-ester shows the stronger absorption, and this would be expected from the fact that this ester is more unsymmetrical than the $\alpha\gamma$-dinitrate. Both isomerides show less absorption than nitroglycerin.

A sample of α-methylin dinitrate was kindly provided by Mr. D. T. Jones, and had been prepared by the nitration of glyceryl α-monomethyl ether (Jones, T., 1919, **115**, 76). This sample had a faint yellow colour, and was fractionally crystallised before use. The absorption spectrum is shown in Fig. 2, and it will be observed that it is slightly more absorptive than glyceryl $\alpha\beta$-dinitrate.

Glyceryl α- and β-mononitrates were prepared by extracting the neutralised, concentrated mother liquors left after the extraction of the dinitrates, as described by Will (*loc. cit.*).

The absorption spectra of glyceryl α- and β-mononitrates in aqueous solution are shown in Fig. 3. The α-compound prepared

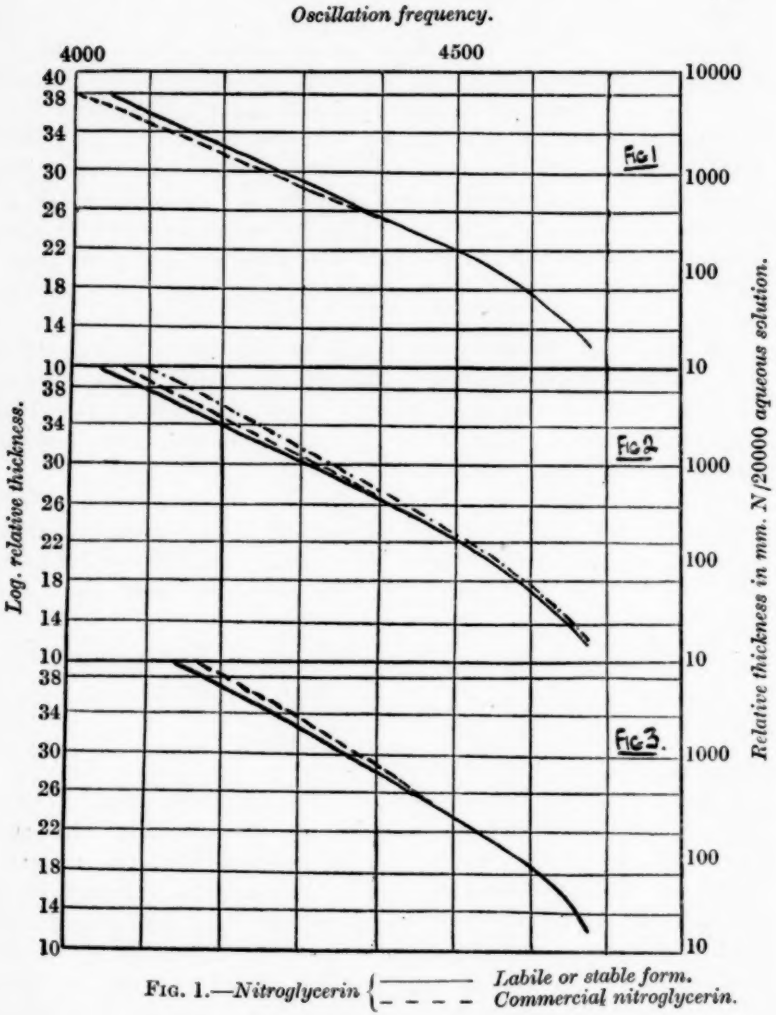

FIG. 1.—*Nitroglycerin* { ——— *Labile or stable form.* - - - - *Commercial nitroglycerin.*

FIG. 2.— { *α-Methylin dinitrate* ——— *Glyceryl αβ-dinitrate* - - - - *Glyceryl αγ-dinitrate* - · - · -

FIG. 3.— { *Glyceryl α-mononitrate* ——— *Glyceryl β-mononitrate* - - - -

by Nef's method gave a spectrum almost identical with that prepared by the direct nitration of glycerol. It will be observed that

both isomerides exhibit less absorption than either the isomeric dinitrates or the trinitrate, and that the unsymmetrical α-isomeride is rather more absorptive than the symmetrical β-isomeride.

The absorption spectrum of glycerol does not appear to have been investigated, and a sample of Hehner's glycerol, used as the standard in the chemical analysis of glycerol used for dynamite, and guaranteed to contain no impurity except water, was examined after drying over phosphoric oxide in a vacuum for four days. It was found that a normal aqueous solution was quite diactinic through a thickness of 10 mm.

It is therefore evident that the substitution of a hydrogen atom of one of the hydroxyl groups of glycerol by a nitro-group produces a profound change in the absorption spectrum, whereas the substitution of one or both hydrogen atoms of the remaining hydroxyl groups by nitro-groups, whilst increasing the general absorption, does not produce nearly so great a change in the absorption spectrum.

Experimental.

Preparation of Pure Nitroglycerin (Glyceryl Trinitrate).

One hundred and eighty grams of Prices's double distilled glycerol were nitrated with a clear, mixed acid of the composition:

	Per cent.
Nitric acid	40·0
Sulphuric acid	57·68
Nitrous acid	0·18
Water	2·14

The nitration was carried out in a large beaker surrounded by a freezing mixture, the glycerol being added at such a rate as to keep the temperature at 10—12° throughout the nitration. The ratio of acid to glycerol was about 7:1. Air stirring was continued for ten minutes after the whole of the glycerol had been added, after which the nitroglycerin was allowed to separate for thirty minutes, no accelerant being employed.

The lower layer of mixed acid was then run off, and the nitroglycerin washed with twelve successive changes of distilled water at 25—30°, the addition of sodium carbonate or any other stabilising substance being avoided. The nitroglycerin was then successively fractionated five times in a freezing mixture. The last fraction, of about 100 grams, was dried in a vacuum over solid potassium hydroxide, and finally obtained as a clear, mobile, faint yellow oil which, after solidification, melted at 13·1°. (Found: N = 18·49. Calc.: N = 18·51 per cent. H_2O = nil.)

Isolation of the Labile and Stabile Forms of Nitroglycerin.—The method adopted for the isolation of the labile and stable forms of nitroglycerin was similar to that described by Hibbert (*loc. cit.*). The labile form was isolated by inoculating nitroglycerin cooled to $-40°$ with a trace of the labile form obtained by cooling two to three drops of nitroglycerin mixed with glass wool to $-40°$, and stirring vigorously. The operation had to be repeated three times before the labile form was obtained, but this was probably due to the fact that the nitroglycerin had been previously frozen. This form appeared to crystallise in the triclinic system, and melted at 2·0°.

The stable form was readily isolated by allowing the nitroglycerin to freeze slowly without inoculation. Large bipyramidal crystals were obtained which melted at 13·1°.

Both forms were allowed to liquefy in a vacuum desiccator over solid potassium hydroxide, and used at once for the spectrographic examination. For the confirmation of the spectrographic results, fresh samples of the labile and stable solid forms were prepared and recrystallised before use.

Commercial Nitroglycerin.—This product had been made by nitrating glycerol (for dynamite) with commercial mixed acid almost identical in composition with that previously described. A trace of hydrocarbon oil had been used to accelerate the separation, and the nitroglycerin had been stabilised by thoroughly washing with dilute sodium carbonate solution followed by several washings with water at 30°. The sample was filtered twice and dried over solid potassium hydroxide in a vacuum desiccator for forty-eight hours. It possessed a distinct brown colour, melted at 12·5°, and contained N = 18·46 per cent. (measured by the nitrometer).

The material was used in this condition for the investigation of the absorption spectrum.

α-Methylin Dinitrate.—This was fractionally crystallised three times and dried in a vacuum over solid potassium hydroxide. The sample examined spectrographically crystallised in white, monoclinic prisms melting at 24·2°, and contained N = 14·23 per cent.

Preparation of the Lower Nitrates of Glycerol.—The method adopted for the preparation of the lower nitrates of glycerol was on similar lines to that described by Will (*loc. cit.*). Two hundred grams of glycerol were nitrated with a clear, mixed acid of the composition:

	Per cent.
Nitric acid	21·76
Nitrous acid	0·06
Sulphuric acid	68·22
Water	9·96

The nitration was conducted exactly as described under the preparation of trinitroglycerin. On allowing the mixture to remain, about 50 grams of nitroglycerin were separated, after which the mixed acid containing the lower nitrates and a little nitroglycerin was diluted and repeatedly extracted with ether after removing a little nitroglycerin which separated on dilution.

The crude dinitrates were twice washed with a little water, filtered, and partly dried. The $\alpha\beta$- and $\alpha\gamma$-dinitrates were separated as described by Will (*loc. cit.*), except that glass wool was used in place of kieselguhr.

The crude $\alpha\gamma$-dinitrate was purified by repeated fractional crystallisation, and about 30 grams were finally obtained in large, water-white, prismatic crystals which melted at 26°. On desiccating over calcium chloride in a vacuum for three days, a pale yellow oil was obtained containing N = 15·30 per cent., and this was identical with the "dinitroglycerin K" described by Will.

The crude $\alpha\beta$-dinitrate showed no tendency to crystallise when cooled at −20° overnight, but, on inoculation, a little $\alpha\gamma$-dinitrate separated. This was repeated until no further traces of the $\alpha\gamma$-dinitrate separated, after which it was dried over calcium chloride in a vacuum. The $\alpha\beta$-dinitrate was obtained in this way as a dark yellow oil containing N = 15·22 (Calc.: N = 15·38 per cent.).

Both dinitrates were kept in a vacuum over solid potassium hydroxide until the solutions were made up for spectrographic examination.

The mononitric esters of glycerol were obtained by evaporating the neutralised mother liquors left after the extraction of the dinitrates, as described by Will (*loc. cit.*). The crude mixture of α- and β-nitrates was easily crystallised by cooling to −20° and vigorously rubbing with a glass rod. Traces of dinitrate were removed from this crude product by dissolving in water and extracting with ether. The separation of the two nitrates was effected by repeatedly washing with a little ether cooled to −20°, when it was found that the β-mononitrate was rather more readily soluble than the α-isomeride.

Both forms were obtained in fine leaflets which, after recrystallising twice from water, gave the following results on analysis:

	M. p.	Found N_2 per cent.	Theoretical.
α-Mononitrate.....	57°	10·2	10·2
β-Mononitrate.....	54°	10·13	

Glyceryl α-Mononitrate prepared from Epichlorohydrin.—A sample of the α-mononitrate was prepared from epichlorohydrin, as described by Nef (*Annalen*, 1904, **335**, 238). It was found that

the conversion of epichlorohydrin into epi-iodohydrin, and the latter into glycide nitrate, proceeded quite normally.

Fifty grams of glycide nitrate were heated at 100° with 40 grams of water for four hours. The product was dried in a vacuum over sulphuric acid, and the crude product melted at 54°. It was purified by recrystallisation from ether, this process being repeated three times, when 40 grams of glyceryl α-mononitrate were obtained. The product melted at 57·5° and crystallised in small, white prisms. When mixed with an equal quantity of the α-mononitrate, prepared by the direct nitration of glycerol, the mixture melted at 58°.

Unsuccessful attempts were made to prepare the α-mononitrate by the direct nitration of glycide, as described by Hanriot (*Ann. Chim. Phys.*, 1879, [v], **17**, 118), but only a very small yield of the α-mononitrate was obtained.

Spectrographic Examination.—The instrument used was a Hilger quartz spectrograph, size C, fitted with a wave-length scale. The iron arc was used as the source of illumination, and the wave-length scale was standardised against the zinc and copper arcs.

All observations were conducted in aqueous solution, the water employed being diactinic up to 2100 Å.U.

Summary.

From an examination of the absorption spectrum of glycerol and its nitric esters, it is evident that:

(1) The labile and stable forms of nitroglycerin are physical isomerides, and both forms are identical in aqueous solution.

(2) Commercial nitroglycerin is more absorptive than pure nitroglycerin.

(3) The order of increasing absorption in aqueous solution is β-mononitrate, α-mononitrate, αγ-dinitrate, αβ-dinitrate, and trinitrate.

(4) α-Methylin dinitrate is rather more absorptive than glycerol αβ-dinitrate.

(5) The displacement of a hydrogen atom of one of the hydroxyl groups of glycerol by a nitro-group produces a much more profound change in the absorption spectrum than the displacement of one or both hydrogen atoms of the remaining hydroxyl groups.

(6) There does not appear to be any numerical proportionality between the number of hydrogen atoms of the hydroxyl groups displaced by nitro-groups and the degree of absorption for any particular dilution.

The author is indebted to Mr. P. A. Baldock, M.Sc., for confirmation of some of the results described in this paper, and also to the Research Committee of Messrs. Nobel's Explosives Co., and particularly to Messrs. Rintoul and Cowie, for the facilities accorded to him for the carrying out and publication of this work.

ARDEER. [*Received, May 26th,* 1919.]

LXIX.—*The Interaction of Acetylene and Mercuric Chloride.*

By DAVID LEONARD CHAPMAN and WILLIAM JOB JENKINS.

ALMOST forty years ago, M. Kutscheroff (*Ber.*, 1881, **14**, 1532, 1540) made the important discovery that hydrocarbons of the acetylene series unite with water in the presence of mercury salts being thereby converted into aldehydes and ketones.

$$CH{:}CH + H_2O = CH_3{\cdot}CHO.$$
$$CH_3{\cdot}C{:}CH + H_2O = CH_3{\cdot}CO{\cdot}CH_3.$$

As is well known, the reaction is of special importance, since it is now employed on a commercial scale for the preparation of acetaldehyde, which is subsequently converted by oxidation into acetic acid.

The mechanism of the action of acetylene on mercury salts in the presence of water and aqueous solutions of acids has been studied by Keiser (*Amer. Chem. J.*, 1893, **15**, 537), K. A. Hofmann (*Ber.*, 1898, **31**, 2217; 1899, **32**, 870; 1904, **37**, 4459), Biltz and Mumm (*Ber.*, 1904, **37**, 4417), Biltz (*Ber.*, 1905, **38**, 133), Biginelli (*Ann. Chimica*, 1898, 16), and Brame (T., 1905, **87**, 427).

Keiser, Hofmann, and Biltz and Mumm investigated the white precipitate obtained by passing acetylene into an aqueous solution of mercuric chloride. Keiser assigned to this substance the formula $ClHg{\cdot}C{:}C{\cdot}HgCl$, which is probably not correct. Hofmann considers that the first product to be formed is a substance having the constitutional formula $(ClHg)_2C{-}{-}CCl_2$ (Hg bridge), this being rapidly hydrolysed to trichloromercuriacetaldehyde, $(ClHg)_3C{\cdot}CHO$. Biltz and Mumm have shown that the white precipitate almost certainly has the constitution of trichloromercuriacetaldehyde, but they regard the evidence for the formation of the intermediate compound assumed by Hofmann as unsatisfactory.

Brame has pointed out that both Hofmann and Biltz failed to notice that Biginelli had observed the formation of small quantities of another substance having the constitution ClHg·HC:CHCl. By the action of acetylene on a solution of mercuric chloride in dilute hydrochloric acid, Brame has prepared the compound in crystalline form and in sufficient quantity to demonstrate some of its properties. He concludes that there seems good reason for believing that the first action of acetylene on either aqueous or dilute acid solutions of mercuric chloride is the formation of the compound ClHg·HC:CHCl by direct addition, together with acetaldehyde. He adds, however, that it remains to be proved whether this additive compound is an intermediate product concerned in the production of acetaldehyde or whether it is a secondary substance derived from the aldehyde.

The chief product of the action of acetylene on a solution of mercuric chloride in dilute hydrochloric acid is acetaldehyde, and it is therefore unlikely that Biginelli and Brame succeeded in converting more than a small proportion of the acetylene into the additive compound of mercuric chloride and acetylene, and it was no doubt chiefly for this reason that Brame was loth to conclude that it was an intermediate compound concerned in the production of acetaldehyde. His reluctance to draw this conclusion may also have been due to his observation that although the crystals were only sparingly soluble in water, they did not begin to separate from the mercuric chloride solution until the acetylene had been acting on the latter for several hours.

We have recently discovered a method whereby a large proportion of the mercuric chloride can be converted into a crystalline compound of the composition $HgCl_2,C_2H_2$. From 72 grams of mercuric chloride, 50 grams of the additive compound were obtained. Unlike the other mercury compounds obtained by the action of acetylene on the salts of mercury, it is dissolved by most organic solvents. In ether or benzene it is very readily soluble, and can be purified by crystallisation from either of these solvents. It is also unique in having a low melting point. In this respect it resembles the mercury alkyl and mercury alkyl haloid compounds, a circumstance that lends support to the view that the constitutional formula of the compound is either

$$ClHg{\cdot}HC{:}CHCl \quad \text{or} \quad \begin{matrix} ClHC \text{---} CHCl \\ \diagdown \quad \diagup \\ Hg \end{matrix} .$$

The acetylene was prepared from calcium carbide, and was collected in two gas-holders of 18 litres capacity. The gas was

circulated for eighteen hours through a saturated solution of mercuric chloride in absolute alcohol (72 grams of mercuric chloride in 75 c.c. of absolute alcohol) through which a slow current of dry hydrogen chloride had been passed for five minutes. After sixteen hours, long, colourless, needle-shaped crystals were deposited in the solution. At the end of the experiment these were collected by the aid of the pump. The mass of the crystals was 10 grams. On pouring the solution into a large volume of water, 40 grams of a white solid were precipitated. This was soluble in ether or benzene; it was crystallised from the latter solvent, and proved to be the same substance as the crystals which had separated from the alcoholic solution during the experiment.

An analysis of the product furnished the following results:

Found: C = 7·93; H = 0·693; Cl = 23·67. Hg = 68·76.

$C_2H_2,HgCl_2$ requires C = 8·07; H = 0·677; Cl = 23·83; Hg = 67·42 per cent.

Owing to decomposition, the melting point could not be accurately determined. It was in the neighbourhood of 113°.

An attempt was made to prepare the compound by passing acetylene through an ethereal solution of mercuric chloride in which dry hydrogen chloride had been dissolved. The acetylene was circulated for twenty hours. At the end of the experiment, the ether was distilled off from the resulting solution, and the solid residue examined. It was almost completely soluble in water, and practically none of it was dissolved in benzene. Therefore the solid residue was almost entirely unchanged mercuric chloride, and very little, if any, of the additive compound could have been formed. It seems likely, therefore, that the compound $HgCl_2,C_2H_2$ is only produced when acetylene is passed into solutions of mercuric chloride in ionising solvents, the compound being formed by the direct addition of the ions $HgCl^{\cdot}$ and Cl' to the unsaturated hydrocarbon.

From the above experiments, it seems probable that the first product of the interaction of acetylene and mercuric chloride is a compound having the constitutional formula ClHg·HC:CHCl. The most interesting property of the compound is its solubility in dry organic liquids, for this circumstance, and the fact that excellent yields of it can now be obtained, suggest that it may prove to be a useful reagent in organic synthesis.

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LXX.—*The Basic Properties of Phenanthraquinone.*

By Joseph Knox and Helen Reid Will.

The investigation of the basic properties of phenanthraquinone was undertaken as part of a scheme for the investigation of the basic properties of oxygen in organic compounds in general. The results in the case of organic acids and phenols are given in a paper by Knox and Richards (this vol., p. 508), which contains also references to the earlier literature on the subject.

The method adopted was to determine the solubility of the organic compound in water and in solutions of mineral acids of increasing concentration. Increasing solubility of the organic compound with increasing concentration of the acid solution is taken to indicate salt-formation in solution. The salt-formation is assumed to be due to the formation of compounds of the oxonium type by the passage of the oxygen from the bivalent to the quadrivalent condition, as explained in the previous communication (*loc. cit.*).

A red, crystalline nitrate of phenanthraquinone is described by Kehrmann and Mattisson (*Ber.*, 1902, **35**, 343), who ascribe to it the constitution $\begin{matrix} C_6H_4\cdot C{:}O \\ | \\ C_6H_4\cdot C{:}O \end{matrix}\!\!>\!\!\begin{matrix} H \\ O\cdot NO_2 \end{matrix}$. They also obtained a red, crystalline compound of phenanthraquinone with sulphuric acid, which, however, was not analysed. They assume that the dark green solution obtained when phenanthraquinone is dissolved in concentrated sulphuric acid contains a salt in which each oxygen atom of the phenanthraquinone is combined with a molecule of sulphuric acid, whilst the red, crystalline compound is regarded as analogous to the nitrate.

In the present investigation, the solubility of phenanthraquinone in water and in various concentrations of sulphuric, hydrochloric, and nitric acids has been determined at 25°. In order that the solubility determinations in the various acids should be comparable, the following method was chosen. A weighed quantity of pure, powdered phenanthraquinone was placed in a glass-stoppered flask and 200 c.c. of the acid solution were added. The flask was allowed to remain in the thermostat at 25° for several days, with frequent shaking, until the solution was saturated. Each concentration of acid was shaken with phenanthraquinone for varying periods until constant results were obtained. The undissolved phenanthraquinone was then rapidly filtered through a tared Gooch crucible,

washed with cold water until free from acid, dried at 100°, and weighed. The solubility in water was determined by shaking at 25° until saturated and evaporating a litre of the saturated solution to dryness on the water-bath and weighing. The following are the results of the solubility determinations. The concentration of the acid solution is given in gram-equivalents per litre and of the phenanthraquinone in grams per litre.

Solubility of Phenanthraquinone in Sulphuric Acid at 25°.

Conc. H_2SO_4	0·00	5·97	6·19	7·00	9·48	11·6	13·7
Conc. $C_{14}H_8O_2$ ...	0·0075	0·0080	0·0085	0·0095	0·012	0·019	0·030

Conc. H_2SO_4	15·1	17·1	18·6
Conc. $C_{14}H_8O_2$ ...	0·043	0·082	0·116

Solubility of Phenanthraquinone in Hydrochloric Acid at 25°.

Conc. HCl	0·00	3·11	4·25	5·12	6·05	6·07	7·20
Conc. $C_{14}H_8O_2$ ...	0·0075	0·012	0·016	0·023	0·029	0·031	0·046

Conc. HCl	8·50	9·25	10·8
Conc. $C_{14}H_8O_2$ ...	0·058	0·088	0·157

Solubility of Phenanthraquinone in Nitric Acid at 25°.

Conc. HNO_3.....	0·00	4·26	4·54	5·02	6·15	6·66	6·70
Conc. $C_{14}H_8O_2$ ...	0·0075	0·049	0·053	0·067	0·099	0·114	0·118

Conc. HNO_3.....	7·20	7·45	8·30
Conc. $C_{14}H_8O_2$ ...	0·157	0·175	0·227

These results are shown graphically in the diagram, in which the ordinates represent the concentration of the phenanthraquinone in centigrams per litre and the abscissæ the concentration of the acid in gram-equivalents per litre.

A high degree of accuracy is not claimed for these solubility determinations. They are, however, sufficiently accurate to show that in every case the solubility increases with increasing concentration of the acid, indicating that phenanthraquinone has basic properties. For the reasons given by Knox and Richards (*loc. cit.*), these basic properties are attributed to the formation of salts of the oxonium type, in which the oxygen becomes quadrivalent.

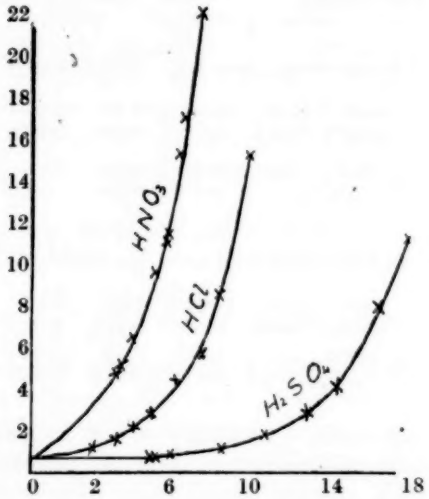
The increase in solubility is greatest in nitric acid and least in sulphuric acid for equivalent concentrations. This was also found to be the case with organic acids and phenols (*loc. cit.*), so that salt-formation occurs most readily with nitric acid and least readily with sulphuric acid.

An attempt was made to determine the concentration of nitric

acid which is in equilibrium with phenanthraquinone and the nitrate, $C_{14}H_8O_2,HNO_3$, according to the reversible reaction

$$C_{14}H_8O_2 + HNO_3 \rightleftharpoons C_{14}H_8O_2,HNO_3.$$

The equilibrium is reached very slowly, however, from the left-hand side. By shaking phenanthraquinone at 25° with various concentrations of nitric acid, it was found that the red nitrate was formed with concentrations of acid in the neighbourhood of 12·5*N*, but that slightly more dilute acid acted very slowly, as indicated by the very slow fall in concentration of the acid with continued shaking. Even with 12·5*N*-acid, the concentration of the acid diminished only slightly, although the red compound was obviously present, since the nitrate is formed on the surface of the phen-



anthraquinone and prevents further action of the acid. The equilibrium was therefore approached from the other side. The red nitrate was prepared by the method described by Kehrmann and Mattisson, and shaken at 25° with various concentrations of nitric acid. When the concentration of nitric acid was below 11·2*N*, decomposition of the nitrate took place comparatively rapidly until the concentration of the nitric acid rose to this value, provided that sufficient nitrate was added to have both solid phases, phenanthraquinone and its nitrate, present at equilibrium. At 25°, therefore, phenanthraquinone and its nitrate, $C_{14}H_8O_2,HNO_3$, are in equilibrium with 11·2*N*-nitric acid.

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LXXI.—*The Solubility of Silver Acetate in Acetic Acid and of Silver Propionate in Propionic Acid.*

By Joseph Knox and Helen Reid Will.

The solubility of silver acetate was determined at 25° in water and in various concentrations of acetic acid, up to about 17*N*, in order to see whether an acid salt was formed under these conditions. In the analogous case of sodium acetate and acetic acid, two acid salts, $C_2H_3O_2Na,C_2H_4O_2$ and $C_2H_3O_2Na,2C_2H_4O_2$, are formed (Farmer, T., 1903, **83**, 1440; Vasilieff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 753; Dukelski, *Zeitsch. anorg. Chem.*, 1909, **62**, 114; Abe, *Mem. Coll. Sci. Eng. Kyōtō*, 1911, **3**, 13; Dunningham, T., 1912, **101**, 431). In the case of silver acetate and acetic acid at 25°, the solubility curve is continuous, indicating that no new phase is formed. The solubility of silver propionate in various concentrations of propionic acid was also determined, and a continuous solubility curve also obtained.

The silver salts were purified by recrystallisation from water, and shown by analysis to be pure. Excess of the salt was shaken with water or varying concentrations of the corresponding acid until constant solubility was obtained. The silver salt in solution was determined gravimetrically as silver chloride, and the acid by titration with sodium hydroxide free from carbonate. The experimental results are as follows. The concentration of the silver salt is given in grams per litre, and that of the acid in gram-equivalents per litre.

Solubility of Silver Acetate in Acetic Acid Solutions at 25°.

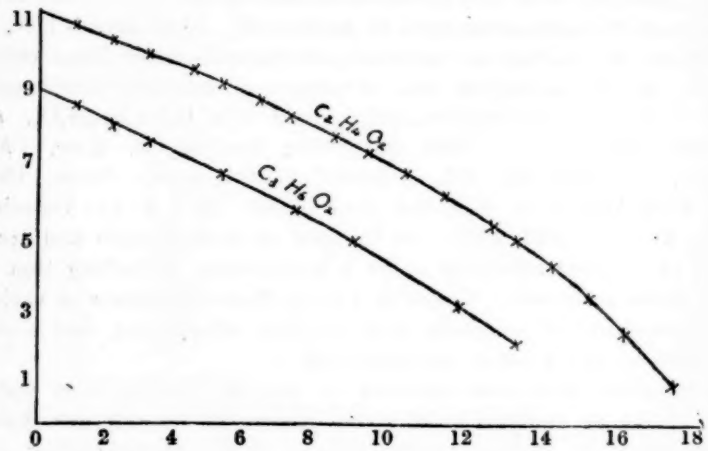
Conc. $C_2H_3O_2Ag$.	11·13	10·73	10·32	9·98	9·52	9·19	8·72	8·29	7·73	7·31
Conc. $C_2H_4O_2$ ...	0·00	1·00	2·00	2·98	4·19	4·98	5·99	6·80	8·01	8·97
Conc. $C_2H_3O_2Ag$.	6·78	6·15	5·33	4·96	4·29	3·43	2·48	1·09		
Conc. $C_2H_4O_2$ ...	9·96	11·02	12·32	12·97	13·97	14·96	15·93	17·28		

Solubility of Silver Propionate in Propionic Acid Solutions at 25°.

Conc. $C_3H_5O_2Ag$.	9·04	8·58	8·01	7·60	6·78	5·78	4·96	3·16	2·17
Conc. $C_3H_6O_2$ ...	0·00	1·00	2·00	2·97	4·95	6·97	8·56	11·40	13·03

The results of the solubility determinations are shown graphically in the diagram, in which the ordinates represent the concentration of the silver salt in grams per litre and the abscissæ the concentration of the acid in gram-equivalents per litre.

The solubility of silver acetate in water at 25° is given by Goldschmidt (*Zeitsch. physikal. Chem.*, 1898, **25**, 91) as 11·18 grams per litre, and by Jaques (*Trans. Faraday Soc.*, 1909, **5**, 225) as 11·07 grams per litre. The value obtained by interpolation from



Raupenstrauch's results at 20° and 30°, recalculated to grams per litre, is 11·21 grams (*Monatsh.*, 1885, **6**, 585). For silver propionate in water at 25°, Goldschmidt (*loc. cit.*) gives 9·04 grams per litre, and the same figure is obtained from Raupenstrauch's results (*loc. cit.*). These values for the solubility of silver acetate and silver propionate in water at 25° agree closely with ours.

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Emission Spectra and Atomic Structure.

A Lecture Delivered before the Chemical Society on March 6th, 1919.

By John William Nicholson.

The invitation of the Council of the Chemical Society to take part in a series of three lectures during the present session is peculiarly acceptable to me, in that it gives me an opportunity to draw attention to certain problems of atomic structure in which further progress can scarcely be hoped for without a more complete co-operation between the physicist and chemist than has hitherto been customary.

The chemist appeals frequently to the physicist, or even to the mathematician, for guidance. I wish to emphasise, and I hope that my remarks will serve to do so, that it is even more a necessity that the real aid to be invoked in the problem which we share in common—that of the elucidation of the nature of the elementary atom—is that of the chemist. It is my belief that this problem will not proceed further towards a satisfactory solution without the joint action of the physicist and the chemist, who have hitherto tended to work in separate channels, without a complete knowledge of their mutual activities. Some of the problems in which co-operation is desirable I hope to indicate, perhaps vaguely, but sufficiently clearly for those of us who have really common interests.

Prof. Soddy has relieved my task very much. One of the pioneers on the chemical side, he gave an account of the bearing of chemistry on the problem of atomic structure which is beyond criticism, and to which nothing further can really be added from that point of view. Some questions were raised on which more could perhaps be said—for instance, the spectra of isotopes, to which I may refer again. As regards his address, I should like to say at the outset that the views therein expressed cannot be contested seriously by the physicist or the mathematician who has worked at the problem of atomic structure.

My own object is to consider this problem from the point of view of spectra. I will endeavour to confine my remarks to the more immediate issues, for the subject of spectra is at present so vast as to transcend any delimitation as a branch of chemistry or of physics. I must consider it only from the point of view of atomic structure, which I have already described as the ultimate aim of both physics and chemistry, an aim only to be achieved by

co-operative effort, and preferably by the existence at the same time of strong chemical and physical schools at one of our leading universities. Prof. Soddy began at the "heavy" end of the periodic table of the elements. I shall, in effect, begin at the "light" end—with hydrogen and helium and possible lighter elements. Before I so begin, however, a few words regarding the nature of spectra are necessary—and my remarks are confined to emission spectra, and not absorption spectra, which, although of supreme importance to the chemist, are less interesting as bearing on the structure of the atom.

Any complete account of the nature of spectral series, as elucidated by experiment, would be quite outside the limits of time of a single lecture. I must perforce neglect various matters, such as satellites of spectrum lines, as of secondary importance. The account of spectra which I give must be accepted as an ideal simplification of existing spectra, to which, nevertheless, theories of atomic structure must conform. Moreover, it is not to be understood that such an account is valid for the heavier elements, the spectra of which exhibit a more complex scheme of relations, but since atomic theories must in practice be illustrated or even confirmed from the lighter and more chemically simple elements, showing the simpler types of spectra, no disadvantage is thereby involved.

Series of spectrum lines will then be regarded as falling into three mutually related sets—the so-called diffuse, sharp, and principal series. The existence of any one of these implies that of the other two, and the lines constituting any one of these series may be single, double, or triple. An element may emit two distinct sets of series, perhaps more. For instance, helium gives three series of single lines and three of doublets. It is a great advantage to work with wave numbers, or numbers of complete wave-lengths in a centimetre, rather than wave-lengths themselves, in the discussion of series, for this procedure enables the relations of the three types of series to be stated very simply. If we proceed along a spectrum series towards the violet, the lines are seen to become closer and closer together until a limit is reached at which two successive members coincide. Lines are never, in fact, visible in the laboratory near this limit, although their convergence towards it can be seen readily enough, the actual limit being a matter of calculation. The diffuse and sharp series tend to the same limit in all cases, and from this limit we can calculate, and thereby predict, the wave-number intervals between the lines of the principal series. The Rydberg-Schuster law gives also the limit of the principal series.

In regard to double lines, the series relations are even more interesting. The wave-number interval between the two members of a doublet is constant along the diffuse and sharp series—the two members form separate series tending to different limits. In a principal series, on the other hand, they tend to the same limit, and the doublets rapidly become narrower towards the violet end of the spectrum.

Our present interest in these questions is mainly confined to the discovery of a chemical atom which can produce a set of ethereal waves the frequencies of which are related in this curious manner.

I will endeavour to summarise some of the more extreme difficulties met at the outset. In the first place, a series contains an infinite number of lines, and if the spectra are in any sense dynamical vibrations of the atom, the frequencies of which are transmitted to our instruments by the ether, the atom must have an infinite number of degrees of freedom. This is not consistent with the very finite number of possible vibrating parts which, from many converging lines of evidence, we are now compelled to assume for its structure—the positive nucleus and some electrons in rotation round it. The only way to surmount this difficulty is, in fact, to postulate that series spectra are derived from the nucleus, and are not a question of the outer electrons. This nucleus must then be endowed with an extremely complex structure. In this way, we might hope to preserve the conception of spectra as dynamical vibrations, and all the lines of the three series might then arise simultaneously from the same atom. We cannot altogether reject this possibility, but if it were more than a possibility, we should be driven to a very disappointing conclusion. For nuclear structure is a thing we may, and often do, speculate about, but it is at the same time practically beyond the power of our experiments. We know, for instance, that α- and β-particles in radioactive phenomena are shot from the nucleus, but nothing we can do appears to have any retarding or accelerating effect on such phenomena or to give a clue to the arrangement of the particles before their emission. We cannot, in fact, influence the nucleus in any effective way, but only its surrounding electrons. Speculative theories of spectra as arising from a nucleus may then be constructed in the future, but there would remain the fundamental difficulty of testing them experimentally. Many phenomena, however, for instance, the Zeeman and Stark effects, and the curious variations shown in the spectra of mixed gases, seem to indicate that the surrounding electrons are vitally concerned and that the nucleus gives us no mode of escape.

Since we cannot have the infinite number of degrees of freedom,

the conception of an infinite number of states of an atom arises with a finite number of spectrum lines—perhaps only one—corresponding with each state. Two lines of the same series are then never given simultaneously from the same atom. This underlies the two theories of production of spectra which have achieved some success, namely, the theories of Ritz and Bohr, on which more will be said later.

The second difficulty to which I shall refer is that all the formulæ which give a useful expression for the series relations of spectral lines serve to show quite conclusively that the frequencies of the lines are simple functions of a quantity to which we can assign any whole-number value we please, each value corresponding with a definite line. Dynamical theory always leads to an expression for the *square* of the frequency, and the frequency itself is a square root which ordinarily does not work out into a simple form. This difficulty is of a type which I do not wish to expound at length now, but it is sufficient to say that a satisfactory theory of spectra as atomic vibrations must lead to an equation giving the frequency itself, and not its square, in the first instance. There is only one known case in which this occurs, namely, the case in which the forces which regulate the vibrations of the atomic electrons are mainly *magnetic*. This is the manner in which Ritz overcomes the difficulty. He found it necessary to postulate the existence of a specific magnetic moment—the *magneton*, in fact—which was invariable, like the electric charge of an electron, from atom to atom. An atom could contain various numbers of magnetons, each corresponding with one of its "states," and each state gave a spectrum line when the electrons of the atom vibrated under the influence of the elementary contained magnets.

This theory of spectra was extraordinarily successful. Its prophecies were verified at every turn, and it was the instrument which, more than any other, has directed the experimental work of spectroscopists into fruitful channels and led to a consolidation of the phenomena of spectra into great generalisations which are now fully established. It led, in fact, to the well-known *combination principle* of spectra on which Bohr's theory was subsequently founded. The defects which are regarded as fatal to it are derived from other considerations than those of spectra. Such problems as the scattering of α- and β-particles by atoms, treated experimentally and compared with the theory developed by Darwin, Bohr, and others, do not appear to be consistent with such fields of magnetic type, although Hicks has had some success in the contrary direction in interpreting the deflections of these particles by a magnetic core of the atom.

I do not propose to say more regarding the existence of magnetic forces within the atom or as regards the existence or non-existence of the magneton itself. There is a vast amount of literature on the subject, which only, in fact, comes into the scope of existing theories of spectra in the manner already briefly indicated. The other theory which has had some success in explaining series spectra is of quite another type, and does not admit such magnetic forces. We shall discuss it later, but shall proceed at present to consider some spectra which do not form ordinary series.

It is difficult to think of an atom as a nucleus of positive electricity with satellite electrons without imagining that the atom is capable of vibrations of a periodic type, and that these vibrations must show themselves in the form of optical wave-lengths. These should, from general considerations, have a frequency which brings many at least into the visible spectrum. The argument is founded merely on the accepted—from many well-established facts—values of the radii, electronic velocities, and so forth. I will proceed to give a short account of some of my own work in this connexion, the data on which it is founded being mainly those of spectroscopic astronomy.

In the first place, one very general result must be stated. It is so frequently ignored in the construction of theoretical atoms that too much emphasis can scarcely be given. Under the inverse square law of attraction or repulsion of elements of electricity, or, indeed, any inverse law at all, coplanar rings of electrons are not possible, in the sense that even an undisturbed atom cannot preserve its configuration. The conclusion may probably be extended to non-coplanar rings.

Rutherford has shown that the nucleus apparently continues to act on electrons with this law at distances less than the atomic radius, and there is much evidence that the electrons continue so to act on each other. If this is confirmed further, the explanations of the phenomena of Röntgen radiation, based on transfer of an electron from one ring to another, will fall to the ground. The subject has many ramifications, and the following statements, capable of logical demonstration, show the chaos in which the physics of the atom is now involved:—

(1) Experiments on scattering of α- and β-particles by atoms indicate that the usual laws of electrical action are valid *inside* the atom. This precludes comparable forces of magnetic origin.

(2) Separate rings of electrons are impossible if (1) is true, and this would annihilate attempts hitherto made to interpret the characteristic X-radiation of atoms, which then can only be a property of the nucleus.

(3) The now accepted dimensions of this nucleus are not consistent with (2). They are also not consistent with the fact that it is capable of sending out β-particles during a radioactive change, for a single β-particle is much larger than a nucleus.

It would be possible to continue such a table of contradictions for a considerable time, and if the quantum theory is invoked, the situation is little better. I do not wish to do more than indicate the position, for more could not be done in a sufficient space. What I wish to make clear is that whilst those who, like Prof. Soddy, discuss radioactive phenomena, proceed from the "heavy" end of the periodic table, any constructive account of spectra must begin at the "light" end.

For the simplest possible elements, there can only be a question of one ring, whatever view is adopted. My own procedure was as follows. Taking the ordinary laws of electrical action, it is possible to work out the frequencies of dynamical vibration of an atom with, say, any number of electrons up to six, in one ring, rotating round a nucleus of any defined strength. The ratios of these frequencies are pure numbers in most cases, although for certain defined vibrations there is a small correction involving the ratio of mass of the electron and nucleus. We may search for vibrations, falling into groups with the prescribed ratios among individual members, in any spectrum that is known to emanate from matter of the simplest form—determined by the fact that no known element heavier than helium, for instance, is indicated as being present—and if such a spectrum is found which falls completely into such groups there is an a priori case for the conclusion that we have given a theory of the spectrum which is satisfactory, and of necessity settles many points of atomic structure.

The nebulæ and the solar corona have been generally believed to consist of the simplest forms of matter. They have always been invoked by speculators on the periodic table and its possible "early" elements, and with much reason. The spectrum of a nebula, for instance, contains only lines of hydrogen and helium, and others which cannot be produced in the laboratory after every possible mode of deriving them from likely elements has been tried. The spectrum of the corona, whilst rich in lines, contains nothing that can be produced in the laboratory. Naturally, in a search for the groups in specified numerical ratios, derived from precisely described atoms, we began with these spectra. The results were startling. The coronal spectrum consists entirely of lines—in number about thirty-six—which all fit precisely into the scheme of ratios for elementary atoms in which the nucleus has a charge $5e$ or $7e$, and five or seven electrons rotating round it, as the case

may be, in its normal state, and smaller or greater numbers in its charged states. The chemical identity of the atom must be regarded as determined by the charge of its nucleus—or its atomic number. The whole coronal spectrum can thus be linked up as the superposed spectra of two chemical substances, and represented by simple formulæ. It was found, moreover, that these formulæ would go further and predict the existence of new and unobserved spectrum lines. A notable instance was the coronium line λ 6374 found by MM. Deslandres and Carrasco some time after the publication of the formula which predicted it, and similar predictions in the case of the spectra of planetary nebulæ have been verified. The corresponding substances in the nebulæ which are invoked as hypothetical entities are the same in kind as those for the solar corona, differing only in nuclear charge or atomic number. It is curious to note that the atomic numbers of the necessary hypothetical atoms for nebulæ are the even numbers 2, 4, 6, and for the corona they are odd numbers, 5, 7. The coronal spectrum appears to come in the main from these hypothetical atoms endowed with strong negative charges, for instance, the atom $7e$ with 9 revolving electrons. This points to an abundance of negative electrons in the corona, unattached to atoms and readily capable of attachment. There is much evidence, at the same time, that the atoms themselves are endowed with very high velocities, and may be a new form of α-particle.

To return to our main argument. What all these atoms share in common is the fact that their angular momenta are simple multiples of a constant unit. Armed with this generalisation, we can calculate the spectrum of any of these hypothetical elements—say one in the nebulæ—from that of another of different chemical nature—say one in the corona. I ventured to put forward the suggestion that this was the real basis of the quantum theory, and that the angular momenta of the electrons in all atoms were related in this simple way to a universal constant of nature, which, being an angular momentum, had the proper dimensions, and even the proper numerical value, as calculation showed, of Planck's unit.

Dr. Bohr, in the theory of series spectra which he subsequently put forward, adopted this generalisation. Prof. Jeans is to address you on the subject the fringe of which we are now touching, so that I will proceed no further, but turn aside to another aspect of importance to chemists. We have seen already that in certain spectrum lines calculated in the way outlined above, there will be a small discrepancy of wave-length due to the fact that the nucleus itself oscillates, as well as the electrons, in the types of vibration producing these lines. Its mass must therefore enter into the

question in these special cases, and it enters as a small term of order m/M, where m is the mass of the electron and M that of the nucleus. From the discrepancies, we can calculate M/m, which, with our practical knowledge of H/m, where H is the mass of the hydrogen atom, gives us M/H, the *atomic weight* of the hypothetical atom. Very concordant results are obtained from these calculations. The atomic weight of coronium, the name given to the hypothetical atom causing the most striking line λ 5303 in the coronal spectrum, is 4·0, suggesting that it may be a helium atom radiating in an unusual manner in an unusual environment; but the atomic weight of the other element there required is 2·0, which corresponds with no known terrestrial element. Again, in the nebulæ, the two most important atoms required give atomic weights 1·3, 3·0, again with no known terrestrial equivalent. Yet, nevertheless, MM. Buisson and Fabry, by their method of determining the mass of a radiating atom from the interference of its radiation, experimentally confirmed the value 3·0, and showed that the element for which our value is 1·3 had an atomic weight greater than, but not much greater than, that of hydrogen. It seems necessary to presume the existence, in circumstances which we perhaps are unable to produce at present in the laboratory—and maintain for a length of time—of such atoms which may not be chemical elements in the sense ordinarily understood by that term.

We have, in fact, two alternatives. Either the atoms in question have not an existence or have not been produced terrestrially, or we have not yet excited them in the laboratory in the appropriate manner to produce such spectra. The latter alternative seems more probable. There is reason to believe that the coronal spectrum at least consists of a somewhat scattered "negative band" spectrum, produced in the presence of an excess of electrons by a very mild form of excitation. However that may be, these spectra, although without doubt the first spectra to receive a strict theoretical basis which is satisfactory, are not *series* spectra as known to us, being in the nature of their relations very analogous to, and without doubt a special case of, band spectra. Series spectra themselves, as defined above, cannot, as we have seen, be ascribed to dynamical vibrations about an atomic condition of steady motion.

Before we proceed to series spectra, we should perhaps state the assumptions involved in the above work. They are, in effect, identical with the conclusions derived by Sir Ernest Rutherford on experimental grounds about six months after the publication of the first paper in which some of these results were obtained. In fact, they can all be included in the statement that the nucleus is at least as small as an electron, and that the law of force between

electric charges is *strictly*—to an extreme order of approximation—that of the inverse square. It is not necessary at this point to emphasise the very definite atomic structure which these results imply. The law of inverse square, the small nucleus, the existence of Planck's constant as a universal angular momentum, are simple examples of what can be deduced. The law of at least some negative spectra of atoms, previously unknown, is another corollary. Many of these deductions have been confirmed by the later experimental work, on quite other ground, of Rutherford and of his colleagues, and have to a large extent become part of the essential basis of Bohr's theory of spectra and its extraordinary consequences, recently worked out by Paschen and others, in regard to the fine structure of lines in the spectrum of hydrogen.

The spectra which we have just described are not series spectra in the ordinary sense of the term. They are in all essentials band spectra. Their production in the laboratory from known materials involves a new type of experiment—an experiment in which a gas of extreme tenuity must be excited by an electric force insufficient to ionise the gas and thus detach an electron, but sufficient to show a "dynamical vibration" spectrum after an exposure of many hours. No such form of excitation has yet been tried in any experimental production of spectra, but it is now being tried by Dr. Merton. It appears to be the only hope of producing some of these elusive astronomical spectra in the laboratory, and thus reaching one of the goals of the astronomical spectroscopist.

It is already clear that series spectra cannot be "dynamical vibration" spectra from the reasons cited above. What are they? The only suggestion which has met with any considerable success is that of Dr. Bohr. Proceeding from the point of view outlined above, he supposes, for instance, that an atom of hydrogen can have one electron rotating with an angular momentum which is any multiple of $h/2\pi$, where h is Planck's constant. He calculates the energy in any such state of rotation—a *stationary* state—and assumes that radiation is emitted in the passage between two such stationary states of amount equal to the loss of energy between the states, and also of amount $h\nu$, where, in accordance with Planck's law, ν is the frequency of the emitted vibration. He thus deduces the hydrogen spectrum as containing the frequencies

$$\nu = B\left(\frac{1}{m^2} - \frac{1}{n^2}\right),$$

where m and n are any integers and B is a universal constant dependent on Planck's constant, the calculated value of which approximates in a remarkable way to Rydberg's universal constant of spectra. The theory does, in fact, reproduce the hydrogen

spectrum, although, of course, that of Ritz, founded on the magneton, did the same, and is too frequently ignored. I wish at this point to make a remark which seems to me essential, and relates to a matter not previously dealt with effectively by theoretical physicists intent upon constructing models of a hydrogen atom which can give the Balmer series spectrum. This spectrum consists of about six lines in the laboratory. The actual spectrum of the hydrogen *atom* contains more than a thousand lines, the rest being the so-called "secondary spectrum." At least six theories of a hydrogen atom have now been given, leading to the Balmer series as its spectrum. But none gives any clue to the origin of the secondary spectrum of hydrogen, which is the real key to the problem of atomic structure, for it is known to be due in the main to the hydrogen *atom*, and not the molecule. I regard the disentanglement of this spectrum into its component bands and series as the most fundamental problem of modern spectroscopy. It is the great simplicity of the formula for the Balmer series which renders it so easy to construct physical theories to account for it. These theories are, nevertheless, unable to carry conviction if they do not provide for a much more extensive spectrum of the hydrogen atom, and no theory has yet even begun this task, which is one of great difficulty in the case of an atom believed to contain only one electron.

I have naturally confined my attention mainly to the more fundamental matters which relate to the simplest chemical atoms. Time is too short to enter into many other interesting points, such, for instance, as the fine structure of the hydrogen lines, which Dr. Merton and I have been elucidating recently. It is now known, for instance, that the Balmer series is a principal series, and not a diffuse series, as hitherto assumed. This result alone has an important bearing on the mechanism of production of this series from an assigned atom. If we were to discuss the spectra of mixed gases or of molecules, a host of problems remains to be solved, and can only be solved by co-operation of the physicist and chemist. To give only one instance, we may ask a question. In a mixture of calcium and barium molecules, with perhaps a temporary association CaBa, what relation would the spectrum of such a molecule have to those of the calcium and barium molecules? The whole question of the spectra of the temporary associations found in vacuum tubes, and analysed by Sir J. J. Thomson's method of "positive rays," remains for solution. All such work will bear on the problem of atomic structure, for an atom is not satisfactory unless it also forms molecules the spectra of which are deducible from that of the atom. No present model of a hydrogen atom appears as yet to have succeeded.

The Quantum Theory and New Theories of Atomic Structure.

A Lecture Delivered before the Chemical Society on May 1st, 1919.

By James Hopwood Jeans.

The problem of the structure of matter falls into two parts: first, the problem of determining the constituent parts of matter, and, second, that of determining the laws according to which these constituent parts move and react with one another.

It has for some time been universally accepted that the fundamental constituents of matter are electrical in their nature, consisting of bodies of infinitesimal size carrying electric charges which are inseparable from them. Briefly speaking, matter is made up of positive and negative charges of electricity. The properties of the bodies carrying the negative charges are fairly well known. These bodies are the negative electrons; they all carry precisely the same charge and have precisely the same mass. They are independent of the chemical nature of the substance to which they belong, and so form standardised and interchangeable parts of all atoms. The same electron which at one instant forms part of an atom of hydrogen may at some future instant form part of an atom of iron; at another instant it may play the rôle of a "free" electron, its motion contributing to the carrying of an electric current through a mass of metal or of gas.

The properties of the positive charges, or "nuclei" as they are commonly called, are known with less certainty. I will try to discuss these properties in their logical order rather than in the chronological order of their discovery. Rutherford has proved that the α-rays emitted by radioactive substances are positively charged particles; he has shown that they all carry the same charge, and that this is equal, numerically, to twice the charge carried by a negative electron. If $-e$ is the charge carried by each negative electron, the α-particle carries a charge $+2e$. Thus an α-particle and two negative electrons would form a system carrying zero charge—an electrically neutral system. The system constituted in this way has been shown by Rutherford to be the normal helium atom. Thus the positive nucleus of the helium atom is simply the α-particle; its charge is $+2e$; its mass is, of

course, the mass of the helium atom minus twice the mass of a negative electron. Since the mass of the helium atom is about 7300 times that of a negative electron, we may say that the positive nucleus carries practically all the mass of the helium atom.

The size of the negative electron is well known. The variation of its mass with its velocity proves that the whole of its mass is electromagnetic, and this circumstance enables us to assign to it the definite radius 2×10^{-13} cm. The size of the helium atom is also known—from the kinetic theory of gases. Its radius is almost exactly 10^{-8} cm., or just about 50,000 times that of the negative electron.

We are led to wonder whether the positive nucleus carries most of the "size" of the atom as well as most of its mass. The answer is provided by experiments on the scattering of α-particles by matter. Imagine a jet of α-particles directed on to a thin sheet of matter. If the α-particles were of the size of helium atoms, it is clear that they would be obstructed at every point by the atoms of the matter, and would not emerge as a jet at all. It has, in point of fact, been found that the majority of the α-particles emerge with their paths only slightly deflected by their encounters with the atoms of the matter, whilst a few have their paths deflected through quite large angles. The inference which must be drawn is that not only are the α-particles excessively minute, but also that the parts of the atoms which are effective in deflecting the paths of the α-particles are themselves excessively minute. The actual amount of scattering observed agrees quantitatively with this conclusion, provided it is assumed that each atom contains only one positive nucleus, its size being infinitesimal compared with the size of an atom, and its charge being approximately proportional to the atomic weight of the matter.

Thus the normal atom is found to consist of a certain number, N, of negative electrons, each of charge $-e$, and a positive nucleus of extremely minute size and of charge Ne. For helium we have already seen that $N=2$, and the question immediately arises as to the value of N for other elements.

This problem has been solved by experiments on the X-ray spectra of the elements. Suppose the elements are arranged in order of their atomic weight, beginning with hydrogen, the lightest, leaving unoccupied gaps where the periodic law suggests that an element remains to be discovered, for example, between tungsten and osmium, and reversing the order of elements where this is demanded by the periodic law, so that, for instance, cobalt is placed before nickel and argon before potassium. The "atomic number" N of any element is that which represents its position in

this series. Thus for hydrogen $N=1$, for helium $N=2$, for lithium $N=3$, for argon $N=18$, for potassium $N=19$, for silver $N=47$, and so on. Then Moseley and others have proved—and I think most physicists are content to accept the proof as conclusive—that the number of negative electrons in the normal uncharged atom of any element is equal to the atomic number N of that element. The charge on the positive nucleus of an atom of an element is accordingly Ne, where N is the atomic number of the element.

This settles, I think, in the opinion of most physicists, finally and incontrovertibly, the problem of determining the ingredients of the atom. The uncharged hydrogen atom consists of a single negative electron of charge $-e$ and a positive nucleus of charge $+e$, the mass of which is something like 1840 times that of the negative electron. The uncharged helium atom consists of two negative electrons and a nucleus of charge $2e$, and so on.

The problem of determining how these constituents are arranged and move inside the atom is still far from complete solution. The material we have to work on consists almost entirely of the spectra of the elements; these provide a mass of data which admit of accurate measurement to five, or even six, significant figures. Knowing the structure of, say, the hydrogen atom, we could calculate its spectrum if we knew its laws of motion, just as Newton, conjecturally knowing the law of gravitation, could calculate what the orbit of a planet ought to be.

Suppose, for instance, that the positive nucleus and the negative electron, which form the normal hydrogen atom, moved according to the ordinary electrostatic law, by which the force varies as the inverse square of the distance. The positive nucleus, being 1840 times more massive than the negative electron, would remain practically at rest, whilst the electron would describe an elliptical orbit about it. The radiation which would be emitted by an electron describing such an orbit can readily be calculated. There would be orbits of all possible sizes, and therefore of all possible periods, so that the emitted radiation would be of all possible frequencies—in other words, the spectrum would be continuous. Since the spectrum of the hydrogen atom consists of sharply defined lines, it is therefore at once clear that the motion in the hydrogen atom is not governed by the ordinary electrostatic laws. Precisely similar reasoning shows that the electron cannot move under any continuous force from the positive nucleus.

Knowing the laws of motion, we could determine the spectrum. Unfortunately, the converse problem is not soluble; knowing the spectrum, we cannot deduce the laws of motion. Some knowledge of a general kind can be obtained—in particular, the laws of motion

are necessarily discontinuous, for continuous laws of motion would lead to a continuous spectrum.

So far, we have considered the atomic spectrum. A somewhat similar situation presents itself when we turn to the consideration of the continuous spectrum of a solid. Except for irregularities arising from imperfect emission of the surface, all solid bodies give the same spectrum at the same temperature. The nature of this spectrum depends on the laws which govern the motion of the electrons by which the radiation is emitted. Different spectra would correspond with different laws of motion, and conversely. Again, if we knew the laws of motion, it would be possible to determine the spectrum.

If the motion of the electrons were governed by the classical laws of mechanics (Newton's laws), it can be shown that the spectrum would be of a very special type—there would be no wave-length of maximum energy, but the energy would increase indefinitely as the wave-length decreased. Thus the total spectral energy at any finite temperature would be infinite, all the energy running into the waves of shortest wave-length. It is therefore clear that the motion of electrons is not governed by the classical laws of mechanics.

In 1901 Planck, starting from a system of laws which differed entirely from the classical laws, and in particular involved the idea of discontinuous motion, arrived at a spectral formula which has since been found to agree extremely well, probably perfectly, with the observed spectrum of a solid. Although Planck's spectral formula, regarded as an expression of a fact of nature, has since gained universal acceptance, his method of deducing it has been widely objected to, mainly on account of his assumption of discontinuous motion. In 1910 I was able to show that Planck's formula could not possibly be arrived at except from a system of laws which involved discontinuities of some kind, and, further, I found that the nature of these discontinuities must necessarily be substantially of the type already assumed by Planck. Almost identical conclusions were enunciated by Poincaré about a year later, together with important additions.

Thus from a study of the continuous spectrum of a solid we conclude that the motion of the radiation-emitting electrons must be of a discontinuous nature. It is, unfortunately, not possible to specify the nature of these discontinuities completely, but a good deal is known. When the electron is executing isochronous vibrations, the total energy of the vibration (potential plus kinetic) must fall into "quanta." The energy may be equal to one quantum, two quanta, etc., but cannot involve fractions of the quantum. Thus

when the energy changes, there must be an instantaneous absorption or emission of a whole quantum of energy. In general, however, when the energy of a vibration changes, the frequency also changes. Now the "quantum" of energy is not the same for all vibrations; it depends on the frequency of the vibration. If ν is the frequency, the quantum is $h\nu$, where h is a universal constant of nature—Planck's "Wirkungsquantum." Thus if an electron jumps from a vibration in which it has n_1 quanta, its frequency being ν_1, to a vibration in which it has n_2 quanta, its frequency being ν_2, it must instantaneously emit an amount of energy $h(n_1\nu_1 - n_2\nu_2)$.

Evidence as to what happens to the energy thus suddenly emitted is provided by the photoelectric phenomenon. To ionise an atom of any substance requires an amount of energy, Q, which depends on the nature of the atom. Now the atoms of any substance can be ionised by light, but only by light the frequency of which is above a critical value ν_0, which again depends on the nature of the atom. This frequency ν_0 is related to the energy Q required for ionisation by the relation $Q = h\nu_0$ (approximately at least). Thus it looks as though light of frequency ν travelled through the ether tied up in some way in bundles of amount $h\nu$—in fact, in quanta. This is Einstein's hypothesis of light-quanta; no doubt it does not express the whole truth, but it must be somewhere near to the truth.

Accepting this hypothesis provisionally, the amount of energy, $h(n_1\nu_1 - n_2\nu_2)$, which we imagined to be set free from one atom will wander through space as a single quantum; in order that it may satisfy the quantum relation (energy $= h\nu$), its frequency must be $n_1\nu_1 - n_2\nu_2$.

On these foundations, Bohr has, with extraordinary skill and acumen, developed his theory of line-spectra. The frequency ν_1 of the original vibration having n_1 quanta must depend on n_1, and similarly ν_2 must depend on n_2. Thus the frequency of the emitted vibration will be expressible mathematically in a formula of the type

$$f_1(n_1) - f_2(n_2),$$

and on giving all possible values to n_1 and n_2, we ought to obtain the whole line-spectrum of the element.

The case of the hydrogen atom is particularly simple. To a first approximation we may consider the massive positive charge as being at rest, and the formula is found to be

$$N\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

This gives exactly the hydrogen spectrum (Balmer's series being given by $n_1=2$, Lyman's series by $n_1=1$, etc.) provided N is equal to Rydberg's constant. Now the theoretical value of N depends only on universal constants of nature. The value of each of these is known to about 1 part in 200, and on inserting these values, the theoretical value of N is found to be equal to Rydberg's constant to about 1 part in 200. There is thus the most brilliant agreement, both quantitatively and qualitatively, between the observed spectrum of hydrogen and the theoretical spectrum predicted by Bohr's theory.

The assumption that the massive positive nucleus stands at rest is only approximately true; actually it will oscillate round the centre of gravity of itself and the negative electron, and this will introduce a correction of the order of M/m, the ratio of the mass of the nucleus to that of the electron. By comparing the theoretical correction with spectroscopic observations, Fowler has deduced for M/m the value 1835, a value which agrees exceedingly well with other determinations of M and m.

Still one other correction of a most fascinating kind must be mentioned. Bohr's theory takes its simplest form when the electron orbits are assumed to be circular; the simple spectral laws are exact for circular orbits. Consistently with the quantum dynamics, however, the electron can also describe a series of elliptic orbits. This possibility gives rise to a new series of frequencies which differ only from those of circular orbits by quantities of the order of $(v/V)^2$, where V is the velocity of light and v that of the electron in its orbit. The theory of relativity makes it possible to calculate the corrections to the frequencies introduced by the ellipticities of the orbits. Sommerfeld has carried the calculation through, and believes that the whole series of frequencies exactly account for the fine structure of the spectral lines. The agreement, so far, is limited to the single line H_α; for this, it is perfect both qualitatively and quantitatively, and I venture to predict that a similar explanation will soon be found of the fine structure of other lines.

This is as far as we can go with any confidence. It seems to me that experimental evidence and abstract reasoning combined practically limit us to one view of the structure and mechanism of the simpler atoms, and this view is confirmed by a large amount of exact spectroscopic evidence. The structure is that of the so-called Rutherford atom; the simpler atoms (hydrogen and helium at least) consist of an extremely minute central nucleus with one or more negative electrons revolving round. The mechanism is

that of Bohr's theory, and is based upon, and governed by, the quantum dynamics.

We cannot, I think, claim to know anything with certainty as to the ultimate structure of the more complex atoms, especially those of radioactive substances, and our definite knowledge of atomic mechanism is practically limited to the few cases in which the atom contains only two constituents—the hydrogen atom, the positively charged helium atom, and possibly also the doubly-charged lithium atom. The "problem of three bodies" has not yet been solved in quantum dynamics any more than in gravitational theory. This is scarcely surprising in view of the fact that the whole quantum theory is wholly a creation of the present century.

We cannot speak with any confidence as to the mechanism of complete molecules other than the monatomic helium molecule; for even the simplest complete molecule, the hydrogen molecule, consists of four constituent parts. If progress continues at its present rate, however, there is every reason for hoping that within a few years the whole scheme of quantum-mechanics will have been unravelled. The problems of valency, stereochemistry, the periodic law, the stability of chemical compounds, their optical and colour properties, and a host of other chemical problems, will then become the province of the mathematician. In spite of the rapidly progressing fusion of all branches of science, the chemist and the mathematician have up to the present remained almost independent. It seems possible that in the near future the chemist will scarcely think of making progress except with the help of the mathematician. In spite of its history of extraordinary triumphs, chemistry is to-day as much an empirical science as electricity was before the time of Maxwell. If once chemistry becomes a mathematical science, it may progress at a rate at present undreamed of.

LXXII.—*Interaction of Mercuric and Cupric Chlorides Respectively and the Mercaptans and Potential Mercaptans.*

By Prafulla Chandra Rây.

Some four years ago, the author ventured to put forth the view that the compounds which mercuric, platinic, and cupric chlorides, respectively, yield with thiocarbamide and thioacetamide, etc., are of the same nature as those obtained by the interaction of these

haloids and real mercaptans, that is, they are chloromercaptides (P., 1914, **30**, 304), and it seemed desirable to undertake a systematic study of the behaviour of mercuric, cupric, and platinic chlorides towards some of the typical mono- and di-mercaptans, namely, ethyl and ethylene mercaptans (dithioethylene glycol) and 2-thiol-5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole.

Ethyl mercaptan yields under normal conditions chloroplatinum mercaptide, $(EtS)_2PtCl$, and under exceptional conditions platinous mercaptide, $(EtS)_2Pt$. Dithioethylene glycol also yields a chloromercaptide of the formula $C_2H_4\langle{}^{S}_{S}\rangle PtCl\cdot S\cdot C_2H_4\cdot SH$. In the formation of this remarkable compound, two molecules of dithioethylene glycol simultaneously take part in the reaction; one atom of chlorine of the platinic chloride remains, however, intact.

The potassium salt of 2-thiol-5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole has been found to be equally reactive towards platinic chloride, and it readily yields mercaptides in which platinum functions both as a triad and a dyad element, as in the case of the simple ethyl mercaptan.

The valency of platinum calls for a few remarks. The salts of the type MX_3 are scarcely represented among the platinum compounds. In the formula $(EtS)_2PtCl$, no doubt platinum may be made to appear as quadrivalent by doubling it. Platinum has its proper place in the eighth or transitional group in the periodic system, which also includes iron and iridium. Now, the chlorides of these metals are represented by the simple formula MCl_3, and not by M_2Cl_6. Moreover, platinum, with the high atomic weight of 194, will scarcely permit of the coalescence of two atoms into the complex ⁝Pt·Pt⁝. Salts containing two atoms of platinum in the molecule have no doubt been described, but they are of a very complex character (Cossa, *Ber.*, 1890, **23**, 2503; Cleve, *Bull. Soc. chim.*, 1872, **17**, 289).

The product of the reaction of mercuric chloride with thiocarbamide has been assigned the formula $HgCl_2,CSN_2H_4$ (Rosenheim and Meyer, *Zeitsch. anorg. Chem.*, 1903, **34**, 62; 1906, **49**, 13). In other words, it has been regarded as a mere additive or molecular compound. From considerations based on analogy, the author suggested that it should be formulated as

$$[NH_2\cdot C(:NH)\cdot S\cdot HgCl]HCl,$$

that is, that it is the product of the reaction of mercuric chloride on ψ-thiocarbamide. The hydrogen chloride which is formed is not liberated in the free state, but is simply fixed by the basic complex. It is well known that formamidine disulphide exists as a salt of a diacidic base, because of the presence of two amino- and

imino-groups. Convincing proof has recently been obtained in support of the above formula. The compound in question has been found to be sufficiently soluble in water to admit of conductivity measurements. If it were an additive one, it would dissociate into its components on dissolution. Now, thiocarbamide is practically a non-electrolyte, and mercuric chloride is very feebly ionised in solution (compare Rây and Dhar, T., 1913, **103**, 8).

The aqueous solution, however, shows an enormous increase in the dissociation, which is of the same order as that of ammonium chloride, proving that the salt is the hydrochloride of a base.

Thiocarbamide may be expected to behave in like manner towards platinic chloride and yield a compound of the same type, thus: $2CS(NH_2)_2 \xrightarrow{PtCl_4} [(NH_2\cdot C(:NH)\cdot S)_2PtCl_2]HCl$. Both Reynolds and Prätorious-Seidler (compare Rathke, *Ber.*, 1884, **17**, 307), however, regard the compound as an additive one of thiocarbamide with platinous chloride, and assign to it the formula $(CSN_2H_4)_2PtCl_2,HCl$ or $(CSN_2H_4)_2PtHCl_3$. That this view is erroneous is evident from another consideration. The platinic chloride on being reduced to the platinous state would set free chlorine, which would in turn act on a portion of the thiocarbamide, and formamidine disulphide hydrochloride would be simultaneously formed;* the derivative in question is, however, free from it.

Cupric chloride is analogous in its behaviour towards thiocarbamide, $CS(NH_2)_2 \xrightarrow{CuCl_2} NH_2\cdot C(:NH)\cdot S\cdot CuCl$. In this case, however, the hydrogen chloride is liberated in the free state and can be detected in the filtrate. This is what might have been expected. The chlorides of mercury, platinum, and cobalt are capable of forming complex compounds with ammonia, amines, and amino-groups, which, on account of their basic character, can fix a molecule of hydrogen chloride, whilst copper, being a more positive metal, does not possess this property.

The view taken above offers also a ready interpretation of the reaction between platinic chloride and thioacetamide, first studied by Kurnakov (*J. Russ. Phys. Chem. Soc.*, 1893, **25**, 613), who formulates the compound as $PtCl_2,4C_2H_5NS,PtCl_4$, that is, as an additive one of four molecules of thioacetamide with one of platinous chloride and another of platinic chloride. This formula, when halved, stands as $PtCl_3,2C_2H_5NS,HCl$, and is in reality $[(CH_3\cdot C(:NH)\cdot S)_2PtCl_2]HCl$, the platinic chloride functioning

* It has been actually found that sulphuryl dichloride, which acts as a mild chlorinating agent, behaves exactly like iodine towards thiocarbamide and yields the hydrochloride of the base.

exactly like mercuric chloride. Thioacetamide here also simply undergoes tautomeric change. One strong argument in favour of the suggested constitution is afforded by the fact that if platinic chloride were actually to be reduced to the platinous form, the available atoms of chlorine would act on two other molecules of thioacetamide. It has already been shown that iodine completely decomposes thioacetamide, the whole of the sulphur being precipitated (T., 1916, **109**, 698). The product in question when treated with carbon disulphide, however, did not yield any sulphur. The corresponding cupric chloride derivative has been found to conform to the formula $CH_3{\cdot}C(:NH){\cdot}S{\cdot}CuCl$; it is, in fact, a chloromercaptide.

The reaction between platinic chloride and thiosemicarbazide is of special interest. The compound obtained has the formula $C_3H_4N_6Cl_2S_3Pt$. Here also a tautomeric change of the thio-compound evidently takes place under the influence of the haloid, resulting in the formation of a cyclic compound with the elimination of a molecule of ammonia, thus:

$$NH_2{\cdot}CS{\cdot}NH{\cdot}NH_2 \longrightarrow NH{:}C(SH){\cdot}NH{\cdot}NH_2 \longrightarrow \begin{matrix} NH{\cdot}C{\cdot}SH \\ \diagdown\!\!\!

few moments, only a deep orange coloration is noticed, but shortly after an orange-yellow precipitate begins to appear. Care should be taken that the platinic chloride is always in sufficient excess. If the conditions of reaction are reversed, that is, if a dilute solution of platinic chloride is added in small quantities at a time to an excess of a concentrated alcoholic solution of ethyl mercaptan with vigorous shaking, for a few minutes the solution remains clear, after which a yellow salt begins to separate, which is very nearly pure platinous mercaptide.

Chloroplatinum mercaptide:

I. 0·050 gave 0·0276 Pt, 0·022 AgCl, and 0·065 $BaSO_4$.* Pt=55·2; Cl=11·33; S=17·85.

II. 0·0502 gave 0·0283 Pt and 0·0675 $BaSO_4$. Pt=56·37; S=18·47.

III. 0·0226 gave 0·0126 Pt. Pt=55·75.

IV. 0·0191 gave 0·0081 AgCl and 0·0242 $BaSO_4$. Cl=10·51; S=17·44.

$C_4H_{10}ClS_2Pt$ requires Pt=55·02; Cl=10·09; S=18·19 per cent.

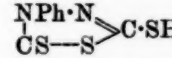
Platinous mercaptide:

0·1317 gave 0·0814 Pt, 0·012 AgCl, and 0·1985 $BaSO_4$. Pt=61·81; Cl=2·25; S=20·71.

$C_4H_{10}S_2Pt$ requires Pt=61·43; S=20·24 per cent.

Contamination with distinct traces of the previous compound, which is invariably formed, accounts for the presence of chlorine.

2-Thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole,



and Platinic Chloride.—To a concentrated aqueous solution of the potassium salt was added, with stirring, a dilute solution of chloroplatinic acid in a thin stream. A yellow precipitate was obtained which, on drying, became orange. Here also, as in the case of ethyl mercaptan, the platinum atom functions as tervalent and bivalent:

0·080 gave 0·0213 Pt and 0·1805 $BaSO_4$. Pt=26·63; S=31·00.

A second preparation gave Pt=25·32.

$(C_8H_5N_2S_3)_3Pt$ requires Pt=22·33; S=33·14.

$(C_8H_5N_2S_3)_2Pt$ requires Pt=30·12; S=29·18.

Mean: Pt=26·23; S=31·16 per cent.

It will thus be seen that here also a compound containing quadri-

* The estimation throughout was effected by fusion with sodium nitrate and sodium carbonate.

valent platinum is never formed, but a mixture of almost equal proportions of the compounds containing tervalent and bivalent platinum.

In the above reactions, the free hydrogen chloride of chloroplatinic acid, acting on a portion of the potassium mercaptide, liberates the corresponding mercaptan, which is insoluble in water, and the available chlorine atoms of the quadrivalent platinum chloride also acting on the potassium mercaptide give rise to the disulphide, which is equally insoluble. The dried precipitate was therefore exhausted first with alcohol and afterwards with benzene in order to extract impurities. The colour of the compound changed from yellow to orange under this treatment.

Dimercaptans and Metallic Haloids.

Dithioethylene Glycol and Platinic Chloride.—A dilute alcoholic solution of platinic chloride was gradually added, with vigorous stirring, to a concentrated alcoholic solution of dithioethylene glycol. A yellowish-brown precipitate was obtained, which was washed with alcohol and dried in a vacuum. It conforms to the formula $C_2H_4\langle{}^{S}_{S}\rangle PtCl\cdot S\cdot C_2H_4\cdot SH$:

0·0788 gave 0·0373 Pt, 0·032 AgCl, and 0·1608 $BaSO_4$. Pt=47·34; Cl=10·05; S=28·03.

$C_4H_9ClS_4Pt$ requires Pt=46·96; Cl=8·58; S=30·93 per cent.

There is reason to conclude that a simpler mercaptide of the formula $C_2H_4\langle{}^{S}_{S}\rangle PtCl_2$ (Pt=54·39; Cl=19·88; S=17·91) is simultaneously formed in small quantities; the higher results for platinum and chlorine and the lower result for sulphur are thus accounted for. Attempts to obtain the chloromercaptide in a purer form proved unsuccessful.

Potential Mercaptans and Metallic Haloids.

Thiocarbamide and Mercuric Chloride.—The components interacted both in alcoholic and in aqueous solution; a copious white precipitate was obtained, which was washed with alcohol and dried in a vacuum. The filtrate was neutral. (Found: C=3·82; H=1·63; N=8·14; Cl=20·45; S=10·03; Hg=56·62. $CH_4N_2Cl_2SHg$ requires C=3·46; H=1·18; N=8·07; Cl=20·46; S=9·22; Hg=57·64 per cent.)

Conductivity Measurement.

V.	*T.*	*μ.*
256	21·5	98·96

There were evidently two ions in solution, and the dissociation is of the order of that of ammonium chloride.

Thiocarbamide and Platinic Chloride.—An acetone solution of thiocarbamide was cautiously added, with constant stirring, to platinic chloride solution. An orange-yellow precipitate was obtained, which was washed with alcohol and dried in a vacuum:

I. 0·0838 gave 0·0365 Pt, 0·0910 $BaSO_4$, and 0·0804 AgCl. Pt = 43·56; S = 14·91; Cl = 23·74.
0·0582 gave 6·6 c.c. N_2 at 33° and 760 mm. N = 12·39.
II. 0·0496 gave 0·0540 $BaSO_4$ and 0·0482 AgCl. S = 14·95; Cl = 24·03.
$C_2H_7N_4Cl_3S_2Pt$ requires Pt = 43·01; S = 14·17; Cl = 23·57; N = 12·40 per cent.

Thiocarbamide and Cupric Chloride.—To an alcoholic solution of cupric chloride was added, with constant stirring, an alcoholic solution of the carbamide. The granular precipitate when dried in a vacuum was white with a faintly blue tint:

0·0608 gave 0·0275 CuO. Cu = 36·09.
0·0443 „ 6·2 c.c. N_2 at 31° and 760 mm. N = 15·41.
0·0588 „ 0·0483 AgCl and 0·0780 $BaSO_4$. Cl = 20·31; S = 18·22.
CH_3N_2ClSCu requires Cu = 36·38; N = 16·12; Cl = 20·44; S = 18·43 per cent.

Thioacetamide and Platinic Chloride.—Thioacetamide in alcoholic solution was added, with stirring, to platinic chloride solution, and the brownish-yellow precipitate was treated as before:

I. 0·0852 gave 0·0360 Pt; 0·0782 AgCl. Pt = 42·26; Cl = 22·79.
II. 0·0334 gave 0·0144 Pt. Pt = 43·11.
0·0813 „ 5·2 c.c. N_2 at 32° and 760 mm. N = 7·01.
III. 0·1457 gave 0·0630 Pt, 0·1697 $BaSO_4$, and 0·1313 AgCl. Pt = 43·83; S = 15·99; Cl = 22·29.
$C_4H_9N_2Cl_3S_2Pt$ requires Pt = 43·20; S = 14·23; Cl = 23·68; N = 6·23 per cent.

Thioacetamide and Cupric Chloride.—The method of preparation was exactly the same as in the preceding case, the salt being almost white. The alcoholic filtrate, when distilled off, was found to contain free hydrogen chloride:

I. 0·0555 gave 0·0250 CuO. Cu = 35·95.
0·0595 „ 4·6 c.c. N_2 at 29·5° and 760 mm. N = 8·57.
II. 0·2818 „ 0·1261 CuO, 0·42 $BaSO_4$, and 0·2250 AgCl.
Cu = 35·78; S = 20·44; Cl = 19·75.

$C_2H_4NClSCu$ requires Cu = 36·59; S = 18·53; Cl = 20·55; N = 8·11 per cent.

Thiosemicarbazide and Platinic Chloride.—A dilute solution of platinic chloride was added to a concentrated aqueous solution* of thiosemicarbazide. In the course of half an hour, a granular precipitate began to be deposited, and the solution was allowed to remain overnight. The granules, when collected and dried, were yellowish-white:

0·2864 gave 0·1171 Pt, 0·1719 AgCl, and 0·387 $BaSO_4$.
Pt = 40·89; Cl = 14·85; S = 18·56.
0·0381 gave 6·2 c.c. N_2 at 30° and 760 mm. N = 17·97.

$C_3H_4N_6Cl_2S_3Pt$ requires Pt = 40·04; Cl = 14·63; S = 19·78; N = 17·31 per cent.

Summary and Conclusion.

(1) Whilst mercuric chloride reacts with a mercaptan to yield a chloromercaptide, thus, $R{\cdot}SH + HgCl_2 = R{\cdot}S{\cdot}HgCl + HCl$, cupric and platinic chlorides generally give mercaptides or mercaptides with only a slight admixture of chloromercaptides.

(2) Platinum in relation to monomercaptanic radicles functions either as tervalent or bivalent.

(3) The above chlorides bring about tautomeric changes in thiocarbamide and thioacetamide. Thiosemicarbazide with platinic chloride also undergoes similar transformation and yields a cyclic degradation product, $\begin{matrix} NH{\cdot}C{\cdot}SH \\ \diagdown\!\!\!\!\diagup \\ N \end{matrix}$.

(4) The chloromercaptides of the potential mercaptans, inasmuch as they contain one or more imino-groups, are capable of fixing a molecule of hydrogen chloride, and in fact are hydrochlorides of complex bases.

CHEMICAL LABORATORY,
COLLEGE OF SCIENCE,
UNIVERSITY OF CALCUTTA. [*Received, June 21st*, 1918.]

* Thiosemicarbazide is almost insoluble in cold alcohol, ether, or acetone.

THE Council has ordered the following letter and report to be printed in the Journal of the Society:

WHINFIELD,
SALCOMBE,
S. DEVON.
June 23rd, 1919.

GENTLEMEN,

I have the honour to submit a Report from the International Committee on Atomic Weights relative to such accounts of experimental work on atomic weights as have been published since their last regular Report of 1916, together with a table which it is suggested should be adopted in place of that now in use.

It will be seen that the Report deals with the atomic weights of hydrogen, carbon, bromine, boron, fluorine, lead, gallium, zirconium, tin, tellurium, yttrium, samarium, dysprosium, erbium, thorium, uranium, helium, and argon.

In the accompanying table for 1920, changes from the values hitherto adopted are recommended for argon, boron, gallium, thorium, and yttrium, and the atomic weight of nitrogen should be changed from 14·01 to the more precise value 14·008, which is probably accurate to within 1 in the third decimal place.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
London.

Report of the International Committee on Atomic Weights for 1919–1920.

The last regular report of this committee, apart from an annual recommendation to continue the use of the table of atomic weights then presented, was published in 1916. The interruption in the series of reports was, of course, due to the world war, which created difficulties of a serious kind among all international organisations. Co-operation with Germany became impossible, partly because of the difficulties of correspondence and partly because of the personal hostilities created by the conduct of the war. There was also an inevitable slackening of scientific activities, and this was well shown by the unusually small number of new researches

in the field of atomic weights. Now that peace is in sight, it seems wise to resume the preparation of these reports, even though they may not be for some time yet quite so truly international as heretofore. The determinations published since the preparation of our last report may now be summarised, as follows:

Hydrogen.—A very thorough investigation by Burt and Edgar* (*Phil. Trans.*, 1916, [*A*], **216**, 393) on the volumetric composition of water has given the volume ratios of H to O as 2·00288 : 1. From this value, taking the normal litre weights of oxygen and hydrogen as 1·42900 and 0·089873 gram respectively, the atomic weight of hydrogen becomes 1·00772, or, rounded off, 1·0077. Guye (*J. Chim. Phys.*, 1917, **15**, 208), from a discussion of Burt and Edgar's data, accepts this value, as lying between the two extremes of 1·00767 and 1·00773. If, however, instead of trusting to the densities of the gases and their physical constants exclusively we take into account the admirable researches of Morley, Noyes, and others upon the synthesis and analysis of water,† the most probable general mean for the atomic weight of hydrogen becomes 1·0078, which differs from the volumetric value by only 1/10,000. That is, the two distinct lines of attack upon the problem agree within the limits of actual uncertainty. For ordinary purposes, the approximate value 1·008 is close enough. It must be remembered that the tables prepared by this committee are for the use, not so much of specialists, as of working chemists in general, and too much refinement will only lead to confusion. No determinations of these or any other constants can be absolute and final. All are subject to errors which may be reduced nearly, but not quite, to insignificance, but never eliminated entirely. For example, in the determination of atomic weights from gaseous densities, it is not possible to guarantee the *absolute* purity of the gases or to avoid errors in weighing, in reductions to a vacuum, or in the values given to the physical constants that are used in the final computations. Some of these errors may be so small as to be negligible, and in the aggregate they may tend either to reinforce or to compensate one another, but their extreme magnitude can be estimated with some approach to accuracy and expressed by means of the usual ± sign. At present, an accuracy to within 1/10,000 is the best we can expect to obtain.‡

* This research was noted in the previous report for 1917. Its review by Guye renders its repetition desirable here.

† Computation by F. W. C.

‡ For an elaborate discussion of sources of error in atomic weight determinations, see Guye and his colleagues (MM. Germann, Moles, and Renard) in *J. Chim. Phys.*, 1916, **14**, 25, 195, 204; 1917, **15**, 60, 360, 405; 1918, **16**, 46.

Carbon—Two investigations on the atomic weight of carbon were reported from the Geneva laboratory in 1918. First, Stahrfoss (*J. Chim. Phys.*, 1918, **16**, 175) determined the density of acetylene, ethane, and ethylene. Acetylene proved to be unsatisfactory, because of its tendency to polymerise. From ethane he obtained the value C=12·006, and from ethylene C=12·004. On account of some uncertainties in the reductions, he prefers, provisionally, the value C=12·00.

Secondly, Batuecas (*J. Chim. Phys.*, 1918, **16**, 322) determined the density of ethane, and reduced his observations by three methods, giving C=12·005, 11·999, and 11·996. The last two, being concordant, he regards as preferable, and their mean, C=11·998, he adopts. It will be remembered that Richards and Hoover, by purely chemical methods, found C=12·005, and a later combination of all determinations published before 1918 gave the chairman of the committee the mean value C=12·0025. For ordinary purposes, the rounded-off value C=12·00 may be used, and is so given in the table.

Bromine.—Three sets of determinations of the molecular weight of hydrobromic acid have been made in Guye's laboratory at Geneva by Moles (*J. Chim. Phys.*, 1916, **14**, 389. See review by Guye in the same number, p. 361), Reiman (*J. Chim. Phys.*, 1917, **15**, 293), and Murray (*J. Chim. Phys.*, 1917, **15**, 334. Reiman and Murray assume H=1·008; Moles prefers 1·0076). The acid used was prepared by several distinct methods, and all gave concordant results, which may be summarised as follows, when H_1=1·0078:

	Mol. wt. HBr.	At. wt. Br.
Moles.....	80·9332	79·9254
Reiman.....	80·932	79·9242
Murray	80·930	79·9222

These values are wonderfully concordant, and the variations are far within the allowable limits of experimental error. In a recent combination, by the chairman of this committee, of all the available data relative to the atomic weight of bromine, the value found was Br=79·9228, in complete harmony with the Geneva determinations. For ordinary purposes, the rounded-off figure 79·92 is enough.

Boron and Fluorine.—In a very original investigation, Smith and Van Haagen (*Carnegie Inst. Washington, Publ.* No 267, 1918) have simultaneously redetermined the atomic weights of boron and fluorine. Their starting point was anhydrous borax, $Na_2B_4O_7$, and their chief difficulty was in insuring the complete dehydration of that compound. The salt was then converted, in a series of

successive experiments, into sodium sulphate, carbonate, nitrate, chloride, and fluoride, which gave eight independent values for boron ranging from B = 10·896 to 10·905; in mean, 10·900. This value was computed with Na = 22·997, Cl = 35·457, S = 32·064, N = 14·010, and C = 12·005. The authors finally discuss all previous determinations, and show wherein they were affected by errors. The new value, 10·900, should be adopted as the most probable.

In this research, sodium fluoride was compared, not only with borax, but also with the sulphate, and the eight values found ranged from F = 19·002 to 19·008; in mean, 19·005. The rounded-off value, F = 19, may be retained for all practical purposes.

Lead.—Œchsner de Coninck and Gérard (*Compt. rend.*, 1916, **163**, 514) have attempted to determine the atomic weight of lead by calcination of the nitrate, and find Pb = 206·98, when $N_2O_5 = 108$. This determination is evidently of no present value. With this exception, the other recent researches relative to this constant have referred to isotopic lead, and the normal element is considered only in comparison with it. Richards and Wadsworth (*J. Amer. Chem. Soc.*, 1916, **38**, 2613), for instance, find for normal lead Pb = 207·183, and Richards and Hall (*J. Amer. Chem. Soc.*, 1917, **39**, 537) give Pb = 207·187, values slightly lower than the accepted 207·20 as determined by Baxter and Grover. Similar determinations by A. L. Davis (*J. Physical Chem.*, 1918, **22**, 631) gave discordant results. As for isotopic lead, its atomic weight is so variable as to show that it is nearly, if not always, a mixture of isotopes, and not a constant which can as yet be placed in the table. The values found have very great significance, but they are far from final.*

Gallium.—By the analysis of carefully purified gallium chloride, Richards, Craig, and Sameshima (*Proc. Nat. Acad. Sci.*, 1918, **4**, 387) find Ga = 70·09 and 70·11. These determinations, however, are only preliminary, but they justify the provisional adoption of the value 70·10. The original values given by the determinations of Lecoq de Boisbaudran vary from 69·70 to 70·12, the last one being very near the new value.

Zirconium.—From the ratios between zirconium chloride and silver, Venable and Bell (*J. Amer. Chem. Soc.*, 1917, **39**, 1598) find Zr = 91·76. Although this determination is regarded as preliminary, the authors, by pointing out sources of error in all previous values, believe the new one to be the most probable. It

* For discussions regarding the atomic weight of isotopic lead, see the Presidential address of Richards before the American Association for the Advancement of Science in December, 1918. Also F. W. Clarke, *Proc. Nat. Acad. Sci.*, 1918, **4**, 181.

seems best, however, to await the complete investigation before changing the value heretofore accepted.

Tin.—Baxter and Starkweather (*Proc. Nat. Acad. Sci.*, 1916, **2**, 718), by electrolyses of stannic chloride, find Sn = 118·703 when Cl = 35·457. This is in complete agreement with Briscoe's determination, Sn = 118·698. The value 118·70 has already been adopted by the committee.

Tellurium.—Staehler and Tesch (*Zeitsch. anorg. Chem.*, 1916, **98**, 1), from careful syntheses of tellurium dioxide, find Te = 127·51, which is confirmatory of the accepted value, 127·5.

Yttrium.—Hopkins and Balke (*J. Amer. Chem. Soc.*, 1916, **38**, 2332), by conversion of Yt_2O_3 into Yt_2Cl_3, find Yt = 88·9. The ordinary sulphate method is shown to be inaccurate. In a later investigation, Kremers and Hopkins (*J. Amer. Chem. Soc.*, 1919, **41**, 718) determined the ratio between yttrium chloride and silver, and found Yt = 89·33. Since this method is the most trustworthy, the value given by it should be adopted. The other sulphate determinations are questionable.

Samarium.—The atomic weight of samarium has been determined by Stewart and James (*J. Amer. Chem. Soc.*, 1917, **39**, 2605) from the ratio between the chloride and silver. The value found is 150·44, which is essentially that given in the table. No change is needed.

Dysprosium.—Engle and Balke (*J. Amer. Chem. Soc.*, 1917, **39**, 67), by conversion of the oxide into the chloride, found Dy = 164·228. Later, by the same method, Kremers, Hopkins, and Engle (*J. Amer. Chem. Soc.*, 1918, **40**, 598) found Dy = 163·83. This discordance, like that already shown for yttrium, led the last-named chemists to determine the ratio between dysprosium chloride and silver, which gave 162·52. The earlier method is discredited, and the last value, rounded to 162·5, seems to be the one best entitled to acceptance.

Erbium.—For this element, by the oxide–chloride method, Wichers, Hopkins, and Balke (*J. Amer. Chem. Soc.*, 1918, **40**, 1615) obtained values ranging from Er = 168·00 to 168·84. The method of determination is thus again shown to be untrustworthy.

Thorium.—In a long series of concordant analyses of thorium bromide, Hönigschmid (*Zeitsch. Elektrochem.*, 1916, **22**, 18) finds Th = 232·152 from the silver ratio and 232·150 from the silver chloride ratio when Br = 79·916. The value Th = 232·15 should be adopted for general use. He also studied thoria from uranium ores which contained ionium. For this mixture, he obtained an atomic weight slightly in excess of 231·50. This may be approximate to the unknown atomic weight of ionium.

Uranium.—The latest series of determinations of the atomic weight of uranium by Hönigschmid and Horovitz (*Monatsh.*, 1916, **37**, 185) was based, like their earlier series, upon analyses of the tetrabromide. Two sets of analyses were made, one upon a bromide which had been fused in bromine vapour, the other in nitrogen. The value obtained ranged from U = 238·04 to 238·16, the latter being in harmony with their former determinations. The rounded figure, 238·2, is given in the table.

Helium.—Taylor (*Physical Rev.*, 1917, **10**, 653), using the microbalance in determining the density of helium, finds He = 4·0008. Guye (*J. Chim. Phys.*, 1918, **16**, 46), in a recalculation of the data, finds He = 3·998. The value 4 should be retained.

Argon.—From the density and compressibility of argon, Leduc (*Compt. rend.*, 1918, **167**, 70) finds A = 39·91. He regards the second decimal as uncertain, and advises the adoption of the rounded value 39·9.

In the following table of atomic weights proposed for 1920, few changes have been made from the values given in the last preceding table. The new values are: A = 39·9, B = 10·9, Ga = 70·1, Th = 232·15, and Yt = 89·33. In addition to these, the atomic weight of nitrogen should be changed from 14·01 to the more precise value N = 14·008. The latter figure represents all the best determinations, and is probably correct to within 1 in the third decimal place. For so small a value, the change is insignificant.

(*Signed*) F. W. Clarke.
T. E. Thorpe.
G. Urbain.

1920.

International Atomic Weights.

	Symbol.	Atomic weight.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	10·9
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·1
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	70·1
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·00
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·20
Lithium	Li	6·94
Lutecium	Lu	175·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·008
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·9
Radium	Ra	226·0
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·06
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·15
Thulium	Tm	168·5
Tin	Sn	118·7
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·2
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	173·5
Yttrium	Yt	89·33
Zinc	Zn	65·37
Zirconium	Zr	90·6

LXXIII.—*The Presence of Aconitic Acid in Sugar-cane Juice and a New Reaction for the Detection of the Acid.*

By Charles Somers Taylor.

Among the non-saccharine substances existing in sugar-juice, Geerligs mentions certain acids which are undoubtedly present. He states, however, that the question of the presence of aconitic acid requires further investigation ("Cane Sugar and the Process of its Manufacture," 1909, p. 51). This acid is generally supposed to have been detected first in the juice of the sugar-cane by Behr (*Ber.*, 1877, **10**, 351). There is no doubt that Behr discovered large quantities of aconitic acid in muscovado sugar and molasses, from both of which he obtained the acid, the composition of which he verified by combustion and also by the formation of a silver salt of known composition. He also appears to have examined the action of lime on invert-sugar in order to find whether the acid can have been formed in the process of manufacture, and states that none of the acid was produced in any of his experiments. As the latter evidence was merely negative, however, he obtained from Cuba some sugar-juice sterilised with phenol, which he examined in Germany. His deduction that aconitic acid was present in this sugar-cane juice was based on the fact that he obtained the lead and acid ammonium salts in their characteristic form. The real criteria of analysis and melting-point determinations were omitted, and he lost the cleanest portion of his acid by accident, whilst some of the partly clean substance obtained by him melted at 167°, or more than 20° below the true melting point of aconitic acid. His evidence, therefore, of the actual existence of this acid in quantity in the juice in its natural state appeared to require further corroboration before it could be said to be conclusive.

The most interesting point to the sugar manufacturer as regards the existence of this acid is that it forms a calcium salt which dissolves readily in cold water, but is almost entirely insoluble in hot. It is therefore liable to be precipitated on the tubes of the evaporating plant unless care is taken to keep the juice hot while filtering.

Experimental.

As it was thought possible that the acid might be a product of disease in the cane, two samples of juice were employed, one from

diseased and one from ordinary cane. Both samples were precipitated with basic lead acetate. The precipitate was then washed, suspended in water, and decomposed in the usual manner with hydrogen sulphide. After filtration, the water was evaporated in a vacuum, and the crystalline residue extracted with ether. The portion insoluble in ether was mostly malic acid. The crude aconitic acid from the ethereal solution was purified by reprecipitating with lead acetate and decomposing the precipitate with hydrogen sulphide. Small quantities of aconitic acid were obtained from the juice of the ordinary canes, but the diseased canes gave a viscid substance by this treatment, from which it was found impossible to crystallise the acid.

Examination of the Acid.—The mean of two determinations of the equivalent weight of the acid gave the value 58·55. The quantities taken were very small, so that the method was subject to large error.

The acid melted and decomposed at 191° (corr.), which is the melting point of aconitic acid. (Found: C=41·38; H=3·95*; C=41·01; H=3·65. $C_6H_6O_6$ requires C=41·38; H=3·45 per cent.)

Qualitative Experiments: A New Colour Test for Aconitic Acid and, indirectly, for Citric Acid.

The usual qualitative tests were carried out with the acid in order to identify it as aconitic acid, although these tests had already been performed by Behr. The calcium salt was obtained as a heavy, white precipitate on boiling a solution of the sodium salt with calcium chloride. It was interesting to note that unless the boiling was protracted, this precipitate dissolved immediately on cooling. After protracted boiling, however, the gelatinous precipitate appeared to change into a crystalline form, which was insoluble even after cooling.

A very delicate test for aconitic acid was discovered in examining the action of acetic anhydride on it. On the addition of this reagent to a small quantity of the acid, a pink coloration appeared, which rapidly turned to deep red and then to magenta. Further heating produced a bluish-green liquid, finally turning to a brown, almost opaque, solution. The red liquid first obtained, if the action is checked by cooling, shows a spectrum entirely in the red, absorbing all other rays almost completely. In the intermediate

* This abnormally high result for hydrogen was probably due to the fact that the combustion was made in India in the middle of the rains, on a day when the air was nearly saturated.

stage, when the magenta liquid was obtained, it appeared to consist of a solution of two coloured substances, namely, a red one which was soluble in water and a blue one which dissolved readily in ether. The two could be easily separated by shaking the acetic anhydride solution with water and ether, when the aqueous layer became red and the ethereal solution blue.

Many attempts were made to isolate these red and blue compounds, but they appear to be exceedingly unstable, being rapidly destroyed by water, acids, or alkalis.

The substance obtained in this way is intensely highly coloured. The intensity of the colour is so great, in fact, that the faintest trace of aconitic acid will produce a strong colour. The minimum quantity necessary to obtain the colour was determined as follows.

One gram of aconitic acid was dissolved in a litre of water, and various fractions of a milligram were obtained by appropriate dilutions and evaporation to dryness in porcelain basins. To the residue a few drops of acetic anhydride were added, and the whole was heated on a water-bath. The results are tabulated below:

Aconitic acid. Milligram.	Colour obtained.
1·0	Intense, appearing almost immediately.
0·1	Strong tinge rather slower in appearance.
0·02	Faint colour taking some time to appear.
0·01	Faint colour just perceptible after some time.

That this reaction was due to aconitic acid alone, and not to the other acids present in sugar-cane juice, was proved positively by examining pure aconitic acid from another source, which gave the same results as that obtained from sugar-cane juice. It was also proved negatively by showing that none of the other acids present in sugar-cane gives the reaction. Citric acid, however, may be detected by the action of acetic anhydride after gentle fusing in a test-tube. By this means, traces of aconitic acid are obtained which at once give the colour reaction. Citric acid itself does not give the reaction.

By this colour test, it was also proved that aconitic acid exists as a salt in sugar-cane juice, and not in the free state. This was done by shaking with ether sugar-cane juice, in the ordinary state and after treatment with dilute sulphuric acid. The ethereal extract in both cases was evaporated to dryness, and the residue heated on a water-bath with acetic anhydride. The extract from the untreated juice gave no reaction whatever, whilst that from the juice which had been treated with sulphuric acid gave the intense red characteristic of aconitic acid.

The Nature of the Colour Reaction between Acetic Anhydride and Aconitic Acid.

That the colour reaction takes place by condensation of the carboxyl groups of the acid is almost certainly proved by the fact that ethyl aconitate, when treated with acetic anhydride, gives no colour whatever.

Treatment of itaconic, citraconic, and mesaconic acids also gave no colour. It was therefore inferred that very little decomposition of the molecule takes place during the reaction, but that the change was probably one of rearrangement of the carbon atoms with, possibly, some removal of water, addition of acetic anhydride, or both actions together.

As has been already mentioned, the actual coloured substance is extremely unstable. Evaporation of the acetic anhydride solution in a vacuum over sodium hydroxide, and subsequent washing with ether, gives a brown substance, which appears to be microcrystalline. No definite crystals were obtained. Analysis of this brown substance gave the following figures:

Found: C = 51·63; H = 2·93.

$C_6H_4O_4$ requires C = 51·43; H = 2·86 per cent.

The substance does not appear to resemble any of the known compounds of this formula. Its deep yellowish-brown colour resembles that of 2:5-dihydroxybenzoquinone, but it appears to be more unstable than that substance. All that can be said for the present, therefore, is that the brown substance has many properties which would point to its having a quinonoid structure, but that this is not proved.

LABORATORY OF THE AGRICULTURAL CHEMIST
TO THE GOVERNMENT OF BIHAR AND ORISSA.

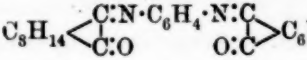
[*Received, January 6th*, 1919.]

LXXIV.—*Studies in the Camphane Series. Part XXXVII. Aryl Derivatives of Imino- and Amino-camphor.*

By MARTIN ONSLOW FORSTER and HANS SPINNER.

THE highest recorded molecular rotation is that of *p*-phenylenebisiminocamphor, which has $[M]_D$ 6173° in a pyridine solution containing 0·624 gram in 100 c.c. (Forster and Thornley, T., 1909, **95**, 942). In this compound there appears to be presented, within a relatively

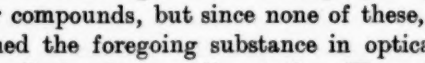
narrow molecular compass, the optimum association of azethenoid groups, conjugated linkings, and a benzene ring,



required for exaltation of the optical activity due originally to the camphor nucleus.

With a view to extending this field of inquiry we prepared a selection of similar compounds, but since none of these, with one exception, approached the foregoing substance in optical activity, they have been described only in a dissertation (Hans Spinner, Zürich, 1912). Several of them having now been prepared by Singh and Mazumder (this vol., 566), who did not have access to the publication in question, we desire to record the properties of the remainder.

The only derivative of this class having optical activity nearly so high as that displayed by *p*-phenylenebisiminocamphor is *pp*-diphenylenebisiminocamphor,



prepared from benzidine and camphorquinone. It occurs in two forms, (1) yellowish-green, melting at 276° and having $[M]_D$ 5565°, and (2) golden-brown, melting at 274° with $[M]_D$ 5360°. In this compound the same exaltation factors are noticeable, but they operate in a slightly less confined molecular environment, which may account for the somewhat diminished optical activity.

It has not been possible permanently to convert either of these compounds into the corresponding derivative of aminocamphor, but the substituted iminocamphors of more simple structure are easily so converted; there is then observed the same profound depression in optical activity already noticed in similar examples (F. and T., *loc. cit.*), as indicated by the following measurements in chloroform at 20°:

	$[\alpha]_D$.	$[M]_D$.	Difference of $[M]_D$.
α-Naphthyliminocamphor	628°	1828°	—
α-Naphthylaminocamphor	115	338	1490°
β-Naphthyliminocamphor	720	2096	—
β-Naphthylaminocamphor	140	411	1685
o-Chlorophenyliminocamphor ...	153	423	—
o-Chlorophenylaminocamphor ...	94	262	161
m-Chlorophenyliminocamphor ...	499	1374	—
m-Chlorophenylaminocamphor ...	118	328	1046
m-Carboxyphenyliminocamphor .	470	1341	—
m-Carboxyphenylaminocamphor .	127	364	975
p-Carboxyphenyliminocamphor...	423	1205	—
p-Carboxyphenylaminocamphor	121	347	858

The one exception is *o*-chlorophenyliminocamphor, because it has by far the lowest optical activity yet recorded in this series, namely, $[M]_D$ 423°, whilst none of the other members, even the *m*- or *p*-chloro-derivative, has $[M]_D$ less than 1000°; it is probable that this abnormality is due to partial saturation of the azethenoid or carbonyl group by supplemental valency of the chlorine atom in an ortho-position.

Although arylamines generally undergo condensation with camphorquinone very readily, some exceptions, in addition to that of *p*-nitroaniline, have been observed; these are *o*-aminobenzoic acid, *o*-aminophenol, 2:4-diaminophenol, 2:4:6-triaminophenol, picramide, picramic acid, 4-nitro-α-naphthylamine, and 5-nitro-α-naphthylamine, from none of which has the corresponding derivative of iminocamphor been obtained.

Experimental.

α- and β-Naphthylaminocamphor, $C_8H_{14}\begin{cases}CH\cdot NH\cdot C_{10}H_7\\ CO\end{cases}$.

α-Naphthyliminocamphor, with $[\alpha]_D$ 628·2° in chloroform, also prepared by Singh and Mazumder (this vol., 573), was shaken in ethereal solution with 10 per cent. potassium hydroxide and zinc dust until the colour had disappeared, when the ether deposited a white residue of α-naphthylaminocamphor on evaporation. Recrystallisation from hot alcohol gave transparent, four-sided prisms melting at 165°:

0·1760 gave 0·5276 CO_2 and 0·1251 H_2O. C = 81·76; H = 7·90.
$C_{20}H_{23}ON$ requires C = 81·91; H = 7·85 per cent.

The product is readily soluble in benzene, chloroform, ethyl acetate, or boiling acetone, moderately so in cold acetone or alcohol; it is insoluble in cold light petroleum, which dissolves it sparingly when boiled. A solution containing 0·1215 gram in 25 c.c. of chloroform gave α_D 1°41′ in the 3-dcm. tube, whence $[\alpha]_D$ 115·5°.

β-Naphthyliminocamphor, with $[\alpha]_D$ 720·5° (compare S. and M., this vol., 573), was treated in the same way, and the resulting β-naphthylaminocamphor crystallised from alcohol in colourless, flattened, four-sided plates melting at 157—158°:

0·2305 gave 0·6896 CO_2 and 0·1631 H_2O. C = 81·59; H = 7·86.

The base is insoluble in cold light petroleum, but dissolves readily in other organic media. A solution containing 0·1255 gram in 25 c.c. of chloroform gave α_D 2°7′ in the 3-dcm. tube, whence $[\alpha]_D$ 140·5°.

o- *and* m-*Chlorophenylaminocamphor*, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_6H_4Cl\\ CO\end{matrix}$.

o-Chlorophenyliminocamphor, with $[\alpha]_D$ 153·4° (compare S. and M., this vol., 572), gave *o*-chlorophenylaminocamphor melting at 148° after crystallisation from hot alcohol, which deposits it in colourless, transparent prisms:

0·2174 gave 0·5508 CO_2 and 0·1431 H_2O. C = 69·10; H = 7·31.
0·1982 „ 0·1013 AgCl. Cl = 12·64.

$C_{16}H_{20}ONCl$ requires C = 69·16; H = 7·26; Cl = 12·77 per cent.

It is readily soluble in organic media other than alcohol and petroleum, which dissolve it less freely. A solution containing 0·1236 gram in 25 c.c. of chloroform gave α_D 1°24′ in the 3-dcm. tube, whence $[\alpha]_D$ 94·4°.

m-Chlorophenyliminocamphor, with $[\alpha]_D$ 498·8° (S. and M., *loc. cit.*), gave *m*-chlorophenylaminocamphor melting at 98—99° after crystallisation from diluted alcohol, whence it separates in colourless aggregates of indefinite structure:

0·1726 gave 0·4368 CO_2 and 0·1129 H_2O. C = 69·02; H = 7·27.
0·2158 „ 0·1106 AgCl. Cl = 12·68.

It is more readily soluble than the isomeride. A solution containing 0·1234 gram in 25 c.c. of chloroform gave α_D 1°45′ in the 3-dcm. tube, whence $[\alpha]_D$ 118·2°.

m- *and* p-*Carboxyphenyliminocamphor*, $C_8H_{14}<\begin{matrix}C:N\cdot C_6H_4\cdot CO_2H\\ CO\end{matrix}$.

Camphorquinone and *m*-aminobenzoic acid in molecular proportion were heated in alcohol during three hours, when the product, after recrystallisation from diluted alcohol, formed pale yellow leaflets melting at 195·5°:

0·3273 gave 15·4 c.c. N_2 at 29° and 763 mm. N = 5·21.

$C_{17}H_{19}O_3N$ requires N = 4·91 per cent.

It is readily soluble in alcohol, acetone, chloroform, ethyl acetate, or boiling benzene, but is insoluble in light petroleum. A solution containing 0·1218 gram in 25 c.c. gave α_D 4°35′ in the 2-dcm. tube, whence $[\alpha]_D$ 470·4°.

The isomeride prepared from camphorquinone and *p*-aminobenzoic acid separated from diluted alcohol in small, brownish-yellow prisms melting at 237° and resembling the *m*-compound in solubility:

0·4210 gave 19·0 c.c. N_2 at 21° and 758 mm. N = 5·15.

A solution containing 0·1217 gram in 25 c.c. of chloroform gave α_D 4°7′ in the 2-dcm. tube, whence $[\alpha]_D$ 422·8°.

m- *and* p-*Carboxyphenylaminocamphor*, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_6H_4\cdot CO_2H\\ CO\end{matrix}$.

The foregoing substances dissolve in aqueous alkali hydroxide, and when the solutions are shaken with zinc dust, filtered, and acidified, the corresponding derivative of aminocamphor is liberated. The *m*-compound separates from diluted alcohol in colourless needles melting at 210—211°:

0·1630 gave 0·4237 CO_2 and 0·1075 H_2O. C = 70·89; H = 7·33.

$C_{17}H_{21}O_3N$ requires C = 71·08; H = 7·32 per cent.

It dissolves readily in acetone, chloroform, or ethyl acetate, less readily in alcohol, being only moderately soluble in benzene and insoluble in petroleum. A solution containing 0·1235 gram in 25 c.c. of chloroform gave α_D 1°53′ in the 3-dcm. tube, whence $[\alpha]_D$ 127·1°.

The *p*-compound crystallises from diluted alcohol in colourless aggregates melting at 239° after slight shrinking and discoloration:

0·1951 gave 0·5081 CO_2 and 0·1287 H_2O. C = 71·03; H = 7·33.

In solubility it resembles the isomeride. A solution containing 0·1207 gram in 25 c.c. of chloroform gave α_D 1°45′ in the 3-dcm. tube, whence $[\alpha]_D$ 120·8°.

p-*Acetylaminophenyliminocamphor*, $C_8H_{14}<\begin{matrix}C:N\cdot C_6H_4\cdot NH\cdot CO\cdot CH_3\\ CO\end{matrix}$.

Camphorquinone and *p*-aminoacetanilide in molecular proportion dissolved in alcohol were heated under reflux during four hours, the product crystallising on dilution in yellow, six-sided plates melting at 211—212°:

0·2166 gave 17·8 c.c. N_2 at 21° and 771 mm. N = 9·53.

$C_{18}H_{22}O_2N_2$ requires N = 9·40 per cent.

It is readily soluble in alcohol, acetone, chloroform, or ethyl acetate, dissolving with difficulty in cold benzene or hot petroleum; it is insoluble in the last-named when cold. A solution containing 0·1220 gram in 25 c.c. of chloroform gave α_D 8°25′ in the 2-dcm. tube, whence $[\alpha]_D$ 862·4° and $[M]_D$ 2570°.

pp-*Diphenylenebisiminocamphor*,

$$C_8H_{14}<\begin{matrix}C:N\cdot C_6H_4\cdot C_6H_4\cdot N:C\\ CO\end{matrix}>\begin{matrix}\\ OC\end{matrix}>C_8H_{14}.$$

Camphorquinone (6·6 grams) and benzidine (3·6 grams) dissolved in alcohol (80 c.c.) were heated under reflux during six hours, when the liquid deposited two distinguishable forms of crystals on cooling;

these were separated mechanically and also by fractional crystallisation, when the less soluble component, formed in preponderating amount, consisted of longitudinal clusters of minute, yellowish-green prisms melting at 276°:

0·2599 gave 0·7606 CO_2 and 0·1785 H_2O. C = 79·81; H = 7·63.

0·2680 ,, 13·4 c.c. N_2 at 22° and 765 mm. N = 5·73.

$C_{32}H_{36}O_2N_2$ requires C = 80·00; H = 7·50; N = 5·83 per cent.

A solution containing 0·1231 gram in 25 c.c. of chloroform gave α_D 11°25′ in the 2-dcm. tube, whence $[\alpha]_D$ 1159·3°.

The more readily soluble modification crystallised in transparent, golden-brown needles melting at 274°:

0·1861 gave 0·5458 CO_2 and 0·1288 H_2O. C = 79·98; H = 7·69.

A solution containing 0·1220 gram in 25 c.c. of chloroform gave α_D 10°54′ in the 2-dcm. tube, whence $[\alpha]_D$ 1116·8°. Both forms yielded benzidine and camphorquinone on hydrolysis with alcoholic hydrochloric acid.

In addition to the foregoing substances we prepared *o*- and *p*-tolyliminocamphor and *p*-benzeneazophenyliminocamphor, which are described by Singh and Mazumder, and in the case of the last-named compound a discrepancy is noticeable. These authors obtained orange needles melting at 129—130° and giving $[\alpha]_D$ 550·4° in chloroform, whilst our product crystallised in silky, red needles melting at 135° and giving $[\alpha]_D$ 677·0°, whence $[M]_D$ 2335°.

p-*Benzeneazophenylaminocamphor*,

$$C_8H_{14}\!<\!\begin{matrix}CH\cdot NH\cdot C_6H_4\cdot N{:}N\cdot C_6H_5\\ |\\ CO\end{matrix},$$

was obtained by shaking an ethereal solution of the iminocamphor derivative with zinc dust and 10 per cent. potassium hydroxide in a closed flask during several hours, when the colour was completely destroyed. On contact with air, however, the ethereal liquid immediately became orange, and on evaporation deposited a brownish-red mass which crystallised from alcohol in lustrous, dark brownish-red, three-cornered plates melting at 170°:

0·1272 gave 0·3538 CO_2 and 0·0826 H_2O. C = 75·86; H = 7·21.

$C_{22}H_{25}ON_3$ requires C = 76·08; H = 7·20 per cent.

From these colour changes it would appear that benzeneazophenyliminocamphor (I) is first reduced to the colourless phenylhydrazinophenylaminocamphor (II; not isolated), which is then oxidised in air

$$C_8H_{14}\!<\!\begin{matrix}C{:}N\cdot C_6H_4\cdot N{:}N\cdot C_6H_5\\ |\\ CO\end{matrix} \qquad C_8H_{14}\!<\!\begin{matrix}CH\cdot NH\cdot C_6H_4\cdot NH\cdot NH\cdot C_6H_5\\ |\\ CO\end{matrix}$$

(I.) (II.)

to benzeneazophenylaminocamphor. Even very dilute solutions of the last-named substance were too dark for polarimetric measurement.

These experiments were carried out at the Royal College of Science, South Kensington, during the later months of 1911.

SALTERS' HALL,
ST. SWITHIN'S LANE, E.C. 4. [*Received, July 3rd*, 1919.]

LXXV.—*The Oxidation of Coal.*

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER.

IN a recent paper ("The Oxidation and Ignition of Coal," T., 1918, **113**, 945) a hypothesis was advanced that the first step in the oxidation of coal is the formation of an additive compound, or complex, of oxygen with one or more of the substances present in coal.

Partington (*Chem. News*, 1919, **118**, 50) has suggested "that this hypothesis, which is of itself not very probable, does not account for the observed results, and that it should be replaced by another hypothesis," based primarily on known physical phenomena, which appears to be somewhat as follows.

(1) The admission of air to newly-won coal, deprived of its occluded gases, results in the physical adsorption of both oxygen and nitrogen on the surface of the coal. The pressure of the air in contact with the coal will at first fall very rapidly for a short period, and will then gradually fall off until adsorption equilibrium is reached. If the adsorbed layer penetrates into the bulk of the adsorbent, this very slow final fall of pressure may go on for a long time.

(2) The adsorbed layer, being at high concentration, may subsequently react with the coal, possibly slowly, with the production of oxides of carbon.

(3) The formation of carbon monoxide and carbon dioxide in a constant ratio at a given temperature is explained on the assumption that carbon monoxide is formed first and subsequently reacts with water-vapour, the "water-gas equilibrium," $CO + H_2O \rightleftharpoons CO_2 + H_2$, being attained.

This hypothesis in principle possesses the great merits of simplicity and of conformity with well-known phenomena. Had it been

possible to account so easily for the facts observed during the oxidation of coal, some such hypothesis would have been chosen in preference to that ultimately adopted.

The phenomena that occur during the oxidation of coal bear a striking resemblance to, and clearly have much in common with, the phenomena of the combustion of carbon.

Rhead and Wheeler (T., 1913, **103**, 461) were faced with a similar difficulty to that which presents itself with coal when attempting to explain the results of their experiments on the combustion of carbon. They found that carbon at all temperatures up to 900°, and probably above that temperature, has the power of pertinaceously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner, it appears, not as oxygen, but as carbon monoxide and carbon dioxide. Rhead and Wheeler concluded, after discussion of their experimental data at some length, that: "No physical explanation alone can account for this 'fixation' of oxygen, but, in all probability, it is the outcome of a physico-chemical attraction between oxygen and carbon. Physical, inasmuch as it seems hardly possible to assign any definite molecular formula to the complex formed, which, indeed, shows progressive variation in composition; chemical, in that no isolation of the complex can be effected by physical means."

In an account of earlier portions of the same research (T., 1912, **101**, 846), the relationship between the carbon monoxide and carbon dioxide produced during the oxidation of carbon had been fully discussed. A comparison of the rates of reaction at different temperatures, between carbon and carbon dioxide, carbon and oxygen, and carbon monoxide and oxygen, with a study of the products of reaction, showed: (1) that some carbon monoxide is produced during the oxidation of carbon at low temperatures under conditions which do not admit of the reduction of carbon dioxide by carbon; on the other hand, (2) carbon dioxide is produced at low temperatures in quantity greater than can be accounted for on the supposition that carbon monoxide is first formed and then oxidised to carbon dioxide. The conclusion follows that when carbon is burnt at low temperatures, carbon monoxide and carbon dioxide are produced simultaneously.

The general conclusion reached by Rhead and Wheeler as regards the mode of combustion of carbon, to account for this simultaneous production of the two oxides, presumes the formation of a complex, as already stated, and partial decomposition of this complex as fresh oxygen molecules became attached, until the carbon becomes "saturated." The products of combustion during this period of satura-

tion are the complex, carbon dioxide, and carbon monoxide. After the carbon has become saturated there is an alternate formation and decomposition of the complex, and the only apparent products of combustion are carbon dioxide and carbon monoxide. These are produced in a fixed ratio dependent on the temperature of reaction. Drying of the oxygen by phosphoric oxide does not affect the formation of the complex, but retards its rate of decomposition (T., 1913, **103**, 1310).

This explanation of the manner of burning of carbon is, we believe, accepted by the majority of chemists. A similar explanation of the manner of burning of coal at low temperatures could be advanced by analogy. To rely solely on such an analogy is, however, scarcely safe; for although there are, in all probability, compounds in coal resembling the carbon molecule in their structure (see Jones and Wheeler, T., 1916, **109**, 709), there is no evidence of the presence of free carbon. Moreover, the fact that the compounds in coal are hydrogenated and that some may yield water on oxidation, introduces a complication from which research on the combustion of carbon is free.

Nevertheless, if the same methods of examining the action of oxygen on coal be followed as with carbon, a similar conclusion will be reached: an hypothesis of physical adsorption of the oxygen, followed by direct formation of carbon monoxide, and, subsequently, of carbon dioxide is inadequate to explain quantitatively the results obtained; although it may, at first sight, afford a plausible explanation of the phenomena qualitatively.

A comparison of the amount of adsorption of inert gases, such as nitrogen, by coal with the amount of oxygen absorbed thereby shows the two actions to be not only of a different order but to be affected by temperature in a different sense.

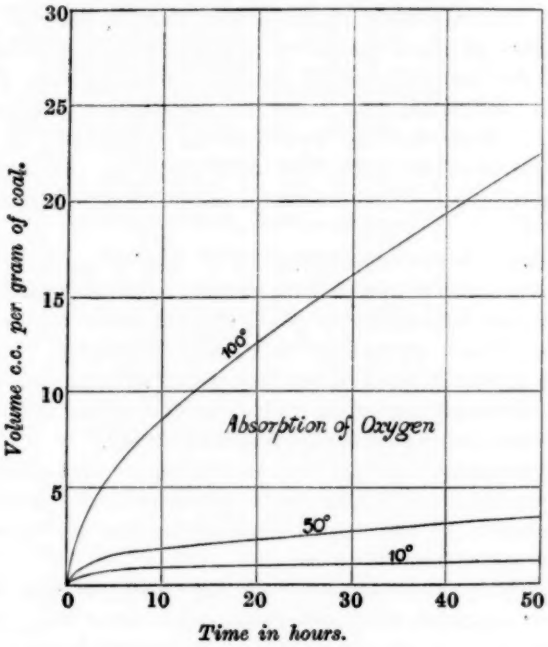
The adsorption of gases by coal has been studied by several chemists; for example, Graham (*Trans. Inst. Min. Eng.*, 1917, **52**, 388) and Katz (*U.S. Bureau of Mines, Tech. Paper* 147; Washington, 1917). Graham obtained the following figures for the quantities of different gases adsorbed or, as he terms it, "dissolved," by the same sample of coal-dust (of 200-mesh fineness):

	Volume of gas adsorbed per gram of coal. C.c measured at N.T.P.				
Temperature.	H_2.	N_2.	CO.	CH_4.	CO_2.
30°	0·068	0·576	0·712	—	8·00
100°	0·038	0·115	0·159	0·476	1·48

As regards oxygen, Graham's own words may be quoted: "The solubility of oxygen—as distinct from the ordinary (chemical) absorption by coal—has also been determined for a sample of

oxidised coal-dust, it being, of course, impossible to determine the solubility in unoxidised coal directly. The sample used had been oxidised for about fourteen days at 100°, and even after this a slight absorption at 30° still took place. For this, however, a correction could be made, and with this it was found that oxygen was soluble in the oxidised sample of coal-dust (of 200-mesh fineness) to the extent of about 40 c.c. per 100 gram when the percentage of oxygen over the dust equalled 100. The solubility of nitrogen in the same sample was found to be equal to approximately 35 c.c. for

FIG. 1.



100 per cent. nitrogen per 100 gram of coal. The figure for the solubility of nitrogen in unoxidised coal for similar concentration was 57·6. It is highly probable, therefore, that the solubility of oxygen in unoxidised coal will be somewhere about 65 c.c. in pure oxygen per 100 gram of coal."

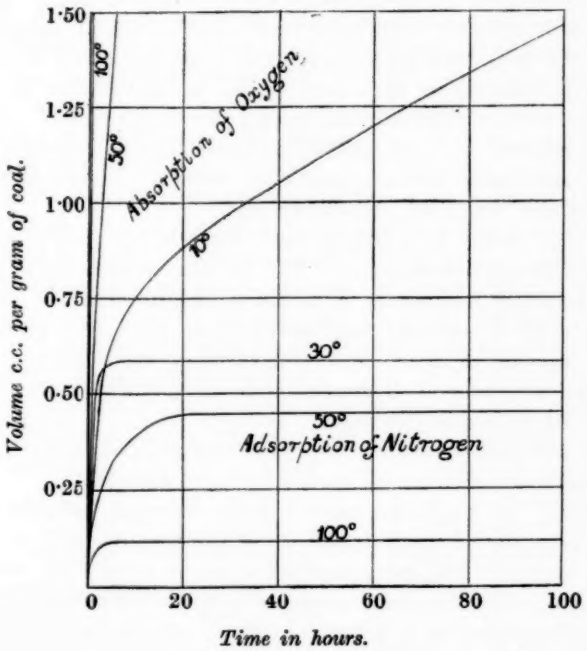
These results for different gases are in agreement with the determinations made of the adsorption of gases by charcoal by Homfray (*Zeitsch. physikal. Chem.*, 1910, **74**, 129), who showed that the amounts adsorbed are proportional to the boiling points of the gases.

In Fig. 1 are given time-volume curves for the absorption of

oxygen by fresh coal (of 10-mesh fineness and deprived of its occluded gases) at 10°, 50°, and 100°; and in Fig. 2 the same curves are reproduced on a different scale for comparison with adsorption curves for nitrogen at 30°, 50°, and 100°. The nitrogen curve at 50° was obtained with a sample of the same coal as was used for the absorption of oxygen; the curves at 30° and 100° are constructed from Graham's data (obtained with a coal of 200-mesh fineness).

Increase of temperature is thus shown to cause a rapid increase in

FIG. 2.



the rate of absorption of oxygen by coal, and an increase in the total amount absorbed (compare also Winmill, *Trans. Inst. Min. Eng.*, 1913, **46**, 3, 559; 1914, **48**, 514). On the other hand, the quantity of a gas physically adsorbed decreases as the temperature is increased.

Even at the ordinary atmospheric temperature the amount of absorption of oxygen by coal is greater than can be accounted for by adsorption phenomena; and the higher the temperature the greater the divergence. Hence the necessity for some such hypothesis as that of complex-formation to account for the facts. Undoubtedly, it is the small but continually renewed amount of

adsorbed oxygen which forms the complex; as with all heterogeneous reactions, the reaction takes place in the condensed layer at the boundary between the two phases; but the complex-formation, and not the adsorption, is specific of the reaction between coal and oxygen.

It is, perhaps, necessary to answer the arguments brought forward in favour of the production of carbon dioxide through the agency of water-vapour, either from carbon monoxide or by direct action on the coal.

The suggested reactions are: $CO + H_2O \longrightarrow CO_2 + H_2$; $C + 2H_2O \longrightarrow CO_2 + H_2$; and, possibly, $2H_2 + O_2 \longrightarrow 2H_2O$. Each of these reactions is known normally to proceed but slowly at temperatures below 400°. With the high concentration of the gases on the coal surface it is conceivable that they might be appreciable at 100° or lower. No such reactions occur during the oxidation of carbon at low temperatures, but, as already indicated, it is desirable not to stress the similarity between coal and carbon. Experiments were therefore made with coal, which showed:

(1) That no trace of hydrogen could be detected in oxygen which had been circulated over coal at 100° during several days.

(2) That (moist) mixtures of carbon monoxide and air circulated over coal at 100° suffered no change other than that due to the action of oxygen on the coal. No hydrogen was formed.

(3) That mixtures of hydrogen and air circulated over coal at 100° suffered no loss of hydrogen.

In each set of experiments the usual formation of carbon dioxide and carbon monoxide, in the ratio 2·4 : 1, took place.

Partington has suggested that "if the reaction between oxygen and coal were one of combination, with the formation of a complex oxide of carbon," the complex should have a definite univariant relationship between vapour pressure and temperature. The complex is not regarded as a definite oxide of carbon or of coal; there most probably are slightly differing compounds in coal to which the oxygen attaches itself, each forming a slightly different product. Probably, also, these oxygen-fixing compounds, which appear to be derived from the cellulosic portions of the original coal-forming materials, have no definite molecular dimensions, but are continuous in structure. The effect of progressive increase of temperature on the complex formed with oxygen by such compounds would be to cause progressive breakdown of their structure with elimination of the simple oxides, the residue requiring further increase in temperature to decompose it further.

Experimental.

The results herein recorded were obtained during the course of an investigation which is still in progress (and, when completed, will form the subject of a communication to this Society), on the relative tendencies to spontaneous ignition of the several distinct portions into which a banded bituminous coal can be separated (see Stopes, *Proc. Roy. Soc.*, 1919, [*B*], **90**, 470; Tideswell and Wheeler, this vol., 619). The particular coal used was the "durain" portion of the Thick Coal Seam, Hamstead Colliery.

The apparatus used, which will be described in detail when the complete research is described, enabled air or oxygen or any mixture of gases to be circulated in a closed system through the coal, which was packed in a reaction-tube the temperature of which could be maintained constant. The progress of the reaction could be followed by the change of pressure within the system and by analysis of the gases.

In all but the experiments with mixtures of carbon monoxide and air, in which a water-bubbler was used, the gases were dried by passage through a calcium chloride tube included in the circuit. The coal was ground so as to pass through a 10×10 and remain on a 60×60 mesh sieve. At the beginning and end of each experiment the coal, in position in the reaction tube, was raised to 200° and exhausted at that temperature.

Typical results for the absorption of pure oxygen at different temperatures are recorded in Fig. 1. Typical results when mixtures of carbon monoxide and air and hydrogen and air were used are as follow:

Carbon Monoxide and Air (7·45 per cent. CO).

Volume of apparatus: 3,300 c.c.
Mean pressure of gases: 660 mm.

	Composition: Expressed as c.c. at 15° and 760 mm.				
	CO_2.	O_2.	CO.	N_2.	H_2.
Initial atmosphere.....	0·9	590	227	2240	nil
Final atmosphere (after circulation during 120 hours at 100°).....	53·4	79	249	2240	nil

Oxygen absorbed = 511 c.c. CO_2 formed = 52·5 c.c.
CO formed = 22 c.c. Ratio CO_2/CO = 2·4.

	CO_2.	O_2.	CO.	N_2.	H_2.
Gases removed from the coal by exhaustion at 200°	26·5	nil	7·7	0·3	nil
Ratio CO_2/CO removed at 200°.....	3·3				

Hydrogen and Air (3·85 per cent. H_2).

Volume of apparatus: 1,200 c.c.
Mean pressure of gases: 560 mm.

	Composition: Expressed as c.c. at 15° and 760 mm.				
	CO_2.	O_2.	CO.	N_2.	H_2.
Initial atmosphere	nil	213·5	nil	788	40·2
After 20 hours at 100° ...	10·52	16·5	3·46	796	40·8
„ 42 „ „ ...	11·20	4·9	4·60	791	39·7
„ 66 „ „ ...	12·00	2·6	4·77	791	40·5

Oxygen absorbed = 211 c.c. CO_2 formed = 12·0 c.c.
CO formed = 4·77 c.c. Ratio CO_2/CO = 2·5.

	CO_2.	O_2.	CO.	N_2.	H_2.
Gases removed from the coal by exhaustion at 200°	3·7	nil	1·2	0·1	nil
Ratio CO_2/CO removed at 200°	3·1				

ESKMEALS,
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LXXVI.—*The Catalytic Reduction of Hydrogen Cyanide.*

By SYDNEY BARRATT and ALAN FRANCIS TITLEY.

WHEN hydrogen cyanide vapour is reduced by gaseous hydrogen in the presence of metallic catalysts, mono-, di-, and tri-methylamine, ammonia, and methane form the bulk of the products. The present paper deals with the relative quantities of the basic substances produced, which were found to vary with the nature and temperature of the catalyst, and with other conditions which are described.

Debus (*Journ. Chem. Soc.*, 1863, **16**, 249) passed a mixture of hydrogen and hydrogen cyanide over platinum black and noticed reduction, accompanied by a considerable development of heat, even at the ordinary temperature. He states that the reaction proceeded vigorously at 110°, the main product being monomethylamine. The rapid decrease in the activity of the catalyst was attributed by him to the formation of a double cyanide of methylamine and platinum, which he isolated.

Linnemann (*Annalen*, 1868, **145**, 38), using the same catalyst, found that the reduction proceeded smoothly at 300°. Although the formation of the double salt was not observed, he found that the catalyst soon lost its activity.

Sabatier and Senderens (*Compt. rend.*, 1905, **140**, 482) investigated the reduction of hydrogen cyanide in the presence of nickel.

They showed that the temperature required for efficient reduction lay between 300° and 400°, or somewhat higher than that required by other nitriles. Ammonia and dimethylamine preponderated in the products isolated.

Experimental.

The larger number of the results described in this paper were obtained with platinum catalysts, but preliminary experiments were also carried out with finely divided iron prepared by the decomposition of ferrous oxalate at 380°.

With the latter catalyst, reduction proceeded at 170° and upwards. At 200°, the basic products isolated by passing the resulting gases through hydrochloric acid contained approximately 45 per cent. of monomethylamine and 55 per cent. of ammonia, with barely a trace of dimethylamine.

The rate of reduction was very low, even at higher temperatures, and after trials under varying conditions, the conclusion was reached that iron was an unsuitable catalyst for the reduction of hydrogen cyanide.

Platinum proved to be considerably more efficient than iron as a catalyst for this reduction, and although it was not found possible to employ the low temperatures suggested by Debus, the activity displayed by the platinum at rather higher temperatures was consistent throughout a long series of experiments.

The catalyst was prepared by soaking blue asbestos fibre in platinum chloride solution. The resulting mass was then dried and reduced in a current of hydrogen at 150°. Catalysts containing from 0·1 to 40 per cent. of platinum on the asbestos were tested. Only those preparations containing more than 10 per cent. of platinum were of practical value in the form of apparatus described below. Those containing less platinum were not sufficiently vigorous, and the catalyst containing 20 per cent. of platinum was most frequently employed. Such variations in the composition of the catalyst affected only the efficiency of the reduction, and not the nature of the products.

Hydrogen cyanide dried by calcium chloride was prepared and liquefied, using the method described by Wade and Panting (T., 1898, **73**, 255); its vapour, mixed with a regulated volume of electrolytic hydrogen, was passed through 22—30 cm. of platinised asbestos in a 1·3 cm. tube heated in a resistance furnace to a temperature measured by a thermo-couple. The alkaline products of the reduction were retained by passage of the gases through hydrochloric acid.

Under these conditions, reduction was first observed at 80°. The velocity of the reaction increases smoothly with rise of temperature to 180°, above which it was fairly rapid; for example, at 200°, 90—100 per cent. of the total hydrogen cyanide in a mixture, passed at the rate of 6 litres an hour, was reduced by 0·3 gram of platinum on 1 gram of asbestos. There appeared to be no advantage in raising the temperature of the catalyst above 220°. The composition of the products, however, was not appreciably affected by carrying out the reduction above 250°.

The products were analysed by the following method. The hydrochloric acid solution of the amines and ammonia was evaporated to dryness, and the solid chlorides were extracted with a known volume of absolute alcohol in excess over that required for complete solution of the amine hydrochlorides. Allowance being made for the slight solubility of ammonium chlorides in alcohol, evaporation of the alcoholic solution gave the total weight of amine hydrochlorides present. These were finally extracted with chloroform to separate the mono- and di-methylammonium chlorides.

From a consideration of the following equations,

$$HCN + 2H_2 = CH_3{\cdot}NH_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$HCN + 3H_2 = NH_3 + CH_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$2CH_3{\cdot}NH_2 = (CH_3)_2NH + NH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$
$$(CH_3)_2NH + CH_3{\cdot}NH_2 = (CH_3)_3N + NH_3 \quad . \quad . \quad . \quad . \quad (4)$$

it will be seen that, in accordance with the law of mass action, reaction (2) might be expected to be favoured by an excess of hydrogen in the gas mixture passing the catalyst. The very reverse, however, took place. If the partial pressure of the hydrogen cyanide was high and approached that required in theory for complete utilisation of the hydrogen (that is, 1 vol. of hydrogen cyanide to 2 vols. of hydrogen), then the products consisted almost entirely of ammonia. As the partial pressure of the hydrogen cyanide decreased, however, the proportion of the methylamines in the product rapidly increased. This continued up to a maximum, above which, however dilute a gas mixture was employed, the methylamine content of the product was constant. The following table and figure illustrate this point.

Composition of gas mixture.	Total methylamines, per cent.	Ammonia, per cent.
1 vol. HCN to 1½ vols. H_2.....	8	92
1 „ „ 4 „ „	33	66
1 „ „ 6 „ „	68	32
1 „ „ 8 „ „	78	22
1 „ „ 15 „ „	80	20

We are unable to offer an explanation of this anomaly.

The "total methylamines" given in the above table consist of mono- and di-methylamines in varying proportions, although trimethylamine is also present in minute quantities. The proportion between mono- and di-methylamine, as would be expected, is also affected by the partial pressure of hydrogen cyanide in the reacting gases. With a concentration of 1 vol. of hydrogen cyanide to 4 vols. of hydrogen, more than half of the total methylamine was dimethylamine. With 1 vol. of hydrogen cyanide to 15 vols. of hydrogen, this decreased to less than 10 per cent. of the total. This is shown in the accompanying figure (curve *A*).

Composition of gas mixture.	Mono- and di-methylamine in the products. Per cent.	
	Mono-	Di-
1 vol. HCN to 4·0 vols. H_2 ...	10	25
1 „ „ 4·4 „ „ ...	15	23
1 „ „ 5·6 „ „ ...	40	20
1 „ „ 6·3 „ „ ...	54	16
1 „ „ 8·0 „ „ ...	66	12
1 „ „ 15·0 „ „ ...	72	8

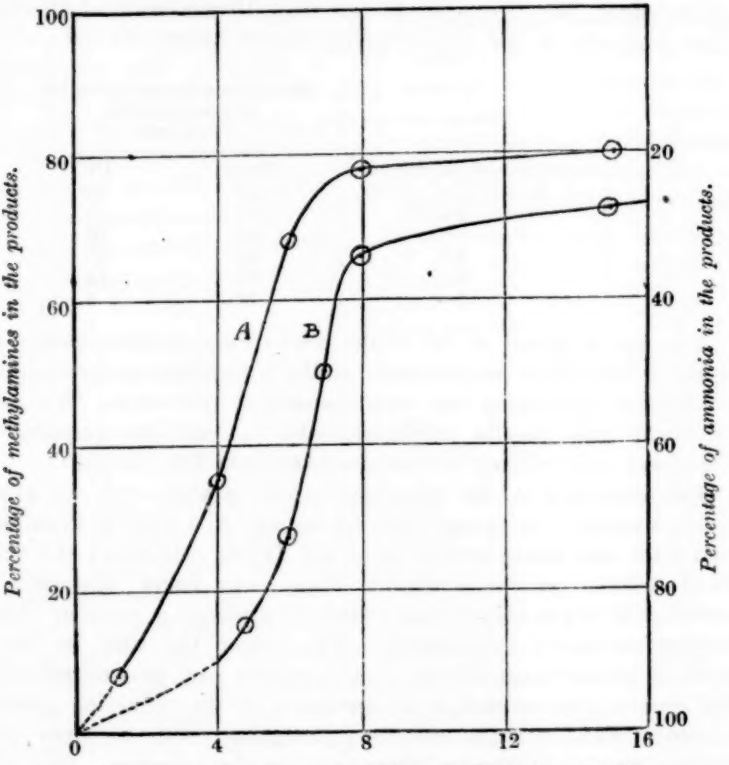
The figures given in the tables above vary within about 5 per cent. in individual experiments, made with different preparations of catalyst containing the same amount of platinum. The tables represent the results obtained with a catalyst prepared as described, and working at temperatures from 180° to 220°.

The alteration in the behaviour of the catalyst with use proved to be unusual. Although the formation of a double cyanide of platinum and methylamine, to which Debus attributed the short-lived activity of his platinum black, was never observed, the activity of our catalysts was found to undergo a peculiar change during successive experiments. The longer the time in use, in spite of identical conditions of temperature and gas concentration, the greater the percentage of ammonia in the reduction products became. This change was very irregular, but occurred more rapidly the less platinum there was on the asbestos. Thus with 0·4 gram of platinum deposited on 1 gram of asbestos, the composition of the products was constant during a period of fifteen hours, but with only 0·1 gram of platinum to the same weight of asbestos, an appreciable difference was noticed after one hour.

Attempts to renew the original behaviour of the catalyst by heating in hydrogen, oxygen, or hydrogen chloride up to 600° were unsuccessful. Treatment with chlorine, however, at 200° for a short period completely renewed the former activity, and, in one or two cases, brought about a slight increase in the yield of methyl-

amine over that obtained with the freshly prepared platinum. In one case, the original percentage of methylamines in the products was 79; during five hours' use of the same catalyst, this decreased to 50, but, after passage of chlorine over the platinum, rose to 86 at the same temperature and with the same concentration of the gases.

Graph illustrating the changes in the products of reduction caused by alterations in the composition of the gas mixture.



Volumes of hydrogen to one volume of hydrogen cyanide.

A. Percentage of methylamine.
B. Percentage of monomethylamine.

At the close of the above work, the conditions were briefly studied, under which methylamine decomposes into hydrogen and hydrogen cyanide.

Liquid monomethylamine was prepared from the hydrochloride and sodium hydroxide, and its vapour passed over a platinum catalyst, prepared as described. It was found that the dehydrogen-

ation, although perceptible at 220°, only proceeds with considerable velocity above 300°, that is, at temperatures more than 100° higher than the minimum required for efficient hydrogenation of the cyanide. This is in accordance with the general rule observed by Sabatier.

Since ammonia and methane, as well as hydrogen cyanide and dimethylamine, were detected in the products, it appears probable that the hydrogen resulting from the dehydrogenation process reduces a further portion of the methylamine (compare Sabatier and Mailhe, *Compt. rend.*, 1917, **165**, 224, 309).

Summary.

(1) Platinum catalyses the reduction of hydrogen cyanide by gaseous hydrogen above 120°, readily above 180°.

(2) The nature of the reduction products, although unaffected by alterations of temperature between 120° and 250°, is dependent on the partial pressure of the hydrogen cyanide in the gas mixture employed, the proportion of monomethylamine increasing to a maximum as this partial pressure is decreased. The secondary reactions which give rise to di- and tri-methylamine are also less marked the lower the pressure of the hydrogen cyanide.

If the concentration of the hydrogen cyanide in the gas mixture is made sufficiently small, a yield of 80 per cent. of total methylamines, and more than 70 per cent. of monomethylamine, can be obtained.

(3) On continued use of a given catalyst, the yield of methylamine diminishes, and is replaced by ammonia. The original behaviour of the platinum is restored by treatment with chlorine.

(4) The dehydrogenation and auto-reduction of methylamine only proceeds with noticeable velocity above 300° in the presence of platinum, and was not observed at 200°, the temperature employed in the majority of the experiments described in this communication.

Our thanks are due to Professor F. Francis for the assistance he gave us during this investigation.

CHEMICAL DEPARTMENT,
THE UNIVERSITY, BRISTOL. [*Received, June 12th*, 1919.]

LXXVII.—*The Chemistry of Burgundy Mixtures.*

By Robert Ludwig Mond and Christian Heberlein.

Although mixtures of sodium carbonate and copper sulphate, generally known as "Burgundy mixtures," have been in use for a number of years as a most effective agent for combating plant diseases of a fungoid character, the chemical reactions which take place when these substances are mixed in solution have hitherto not received much attention.

Abegg ("Handbuch der anorg. Chemie," II., i, 633) states: "From solutions of copper sulphate, sodium carbonate at ordinary temperatures gives a greenish-blue colloidal precipitate of varying composition, which contains absorbed alkali carbonate. With excess of copper sulphate the precipitate also contains basic copper sulphate. With equivalent quantities of the components the gel contains copper and carbon dioxide in the ratio $2CuO:1CO_2$.

If the precipitates are left with the mother liquor they become crystalline and change into the green, granular basic carbonate, $3CuCO_3,3Cu(OH)_2,H_2O$.

In contact with a concentrated solution of sodium carbonate, the gel is transformed into Deville's blue, crystalline double carbonate, $Na_2CO_3,CuCO_3,3H_2O$."

This statement pointed to a complexity of reactions which required further elucidation. The fact that a colloidal solution was formed appeared to us to have an important bearing on the fungicidal properties of the material in question, and we asked Prof. Barker, of the University of Bristol, to investigate the relative advantages of the colloidal over the crystalline state. His preliminary results are embodied in a very interesting paper, which will be published in the University's Annual Report.

In spite of the highly significant work which has been done by Pickering (T., 1909, **95**, 1409) and Ravaz ("Le Mildion," Paris, Masson and Cie., 1914) on Burgundy mixture, we found the problem more complicated than they had assumed, and we proceeded to carry out our investigations on the following lines:

(1) The main reactions between copper sulphate and sodium carbonate were quantitatively studied with various ratios of the components.

(2) The reaction between copper sulphate and sodium hydrogen carbonate was examined.

(3) The free carbon dioxide and the carbon dioxide in the precipitate were estimated, and the ratio $CuO:CO_2$ in the precipitate was determined.

(4) The solvent action of carbonic acid was studied.

(5) The basic sulphate was determined in various mixtures to ascertain the ratio $CuO:SO_3$ and $CuO:CO_2:SO_3$.

(6) The absorbed sodium carbonate was estimated.

(7) The causes and reactions of the change from the colloidal precipitate to malachite were investigated.

(1) *The Main Reactions between Copper Sulphate and Sodium Carbonate.*

The mixtures were generally made at 15° by dissolving 4 grams of crystallised copper sulphate in 200 c.c. of water and a varying amount of crystallised sodium carbonate in 200 c.c. of water, and then pouring the two solutions simultaneously into a third beaker, thus avoiding any excess of one reagent over the other. The mixtures were tested (*a*) with litmus paper; (*b*) the copper in solution was estimated by electrolysis; (*c*) a filtered portion of the mixture was tested directly with ferrocyanide; (*d*) a filtered portion, after boiling and filtering, was tested with ferrocyanide; (*e*) the free sodium hydrogen carbonate and the basic copper sulphate in solution were titrated with *N*/10-hydrochloric acid, using methyl-orange as indicator; (*f*) the free sodium carbonate was titrated with phenolphthalein as indicator.

The various mixtures and the results of the analyses are tabulated in table I.

It will be noticed that a theoretical mixture of equivalent amounts of copper sulphate and sodium carbonate, namely, 4 grams of $CuSO_4,5H_2O$: 4·58 grams of $Na_2CO_3,10H_2O$, although reacting alkaline towards litmus and methyl-orange, contains a considerable amount of copper in solution. A mixture with 7·38 grams of sodium carbonate (Pickering's mixture) contains the minimum amount of soluble copper. Larger amounts of sodium carbonate cause the formation of complex compounds containing electronegative copper.

From curve 1 in Fig. 2 it will be seen that the solution is alkaline towards methyl-orange after a small addition of sodium carbonate, due to soluble basic copper sulphate. The curves in this figure show three distinct stages. Up to 4·25 grams of sodium carbonate the solution contains free copper sulphate and an increasing amount

TABLE I.

Copper sulphate. Grams.	Crystalline sodium carbonate. Grams.	Molecular ratio, $CuSO_4 : Na_2CO_3$.	Litmus reaction.	Potassium ferrocyanide. After filtration.	Potassium ferrocyanide. After boiling.	Copper in solution. Grams per litre.	Copper in solution. Per cent. on total.	Titration with N/10-HCl. C.c. for Na_2CO_3.	Titration with N/10-HCl. C.c. for $NaHCO_3$.	In solution in total mixture. Grams. Na_2CO_3.	In solution in total mixture. Grams. $NaHCO_3$.	Percentage in solution on total carbonate used, = 100 per cent. as Na_2CO_3.	Percentage in solution on total carbonate used, = 100 per cent. as $NaHCO_3$.	Percentage in solution on total carbonate used, = 100 per cent. as $Na_2CO_3 + NaHCO_3$.	
4·0	2·13	1 : 0·46	acid	Cu	Cu	1·240	50·22	—	0·22	—	—	—	—	—	
4·0	3·18	1 : 0·70	,,	,,	,,	0·72	29·16	—	0·38	—	—	—	—	—	
4·0	4·15	—	neutral	,,	,,	—	—	—	0·59	—	0·1982	—	7·9	7·9	
4·0	4·20	—	,,	,,	trace Cu	—	—	—	0·68	—	0·2413	—	9·7	9·7	
4·0	4·25	1 : 0·93	,,	,,	nil	0·24	9·6	—	0·64	—	0·2150	—	8·6	8·6	standard mixture.
4·0	4·50	1 : 0·98	faintly alkaline	,,	,,	0·20	8·0	—	0·81	—	0·2645	—	10·0	10·0	
4·0	5·0	1 : 1·10	,,	,,	,,	0·12	4·8	—	1·29	—	0·4389	—	14·9	14·9	
4·0	6·38	1 . 1·39	,,	,,	,,	0·04	1·6	—	3·12	—	1·080	—	28·8	28·8	
4·0	7·38	1 : 1·62	,,	trace Cu	,,	0·005	0·2	—	4·63	—	1·5946	—	36·8	36·8	
4·0	7·45	—	distinctly alkaline	,,	,,	—	—	—	4·54	—	—	—	—	—	
4·0	7·52	—	,,	,,	,,	—	—	0·10	4·57	—	—	—	—	—	
4·0	7·59	—	,,	,,	,,	—	—	0·15	—	—	—	—	—	—	
4·0	7·66	—	,,	,,	,,	—	—	0·15	4·75	—	—	—	—	—	
4·0	7·94	—	strongly alkaline	,,	,,	—	—	0·43	4·84	—	—	—	—	—	
4·0	8·5	1 : 1·86	,,	,,	,,	0·01	0·4	1·54	4·84	0·3347	1·6669	10·6	31·6	42·2	
4·0	12·75	1 : 2·79	,,	Cu	Cu	0·02	0·8	7·81	5·46	1·6971	1·8804	35·9	25·1	61·0	

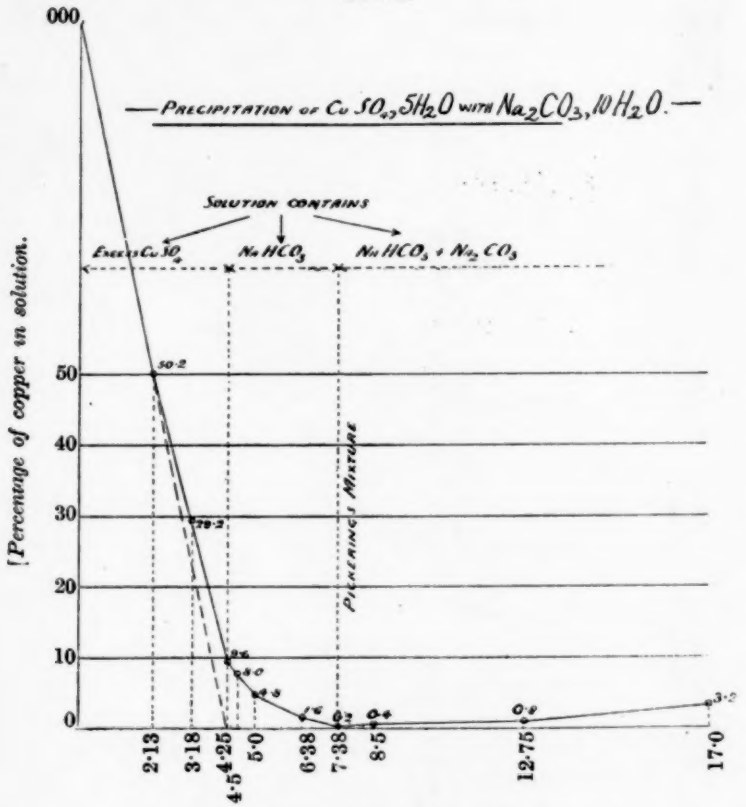
TABLE I (*continued*).

Copper sulphate. Grams.	Crystalline sodium carbonate. Grams.	Molecular ratio, $CuSO_4 : Na_2CO_3$.	Litmus reaction.	Potassium ferrocyanide. After filtration.	Potassium ferrocyanide. After boiling.	Copper in solution. Grams per litre.	Copper in solution. Per cent. on total.	Titration wit *N*/10-HCl. C.c. for Na_2CO_3.	Titration wit *N*/10-HCl. C.c. for $NaHCO_3$.	In solution in total mixture. Grams Na_2CO_3.	In solution in total mixture. Grams $NaHCO_3$.	Percentage in solution on total carbonate used, = 100 per cent. as Na_2CO_3.	Percentage in solution on total carbonate used, = 100 per cent. as $NaHCO_3$.	Percentage in solution on total carbonate used, = 100 per cent. + as Na_2CO_3 $NaHCO_3$.	
4·0	17·0	1 : 3·72	strongly alkaline.	Cu	Cu	0·08	3·2	13·99	6·19	3·0400	2,1318	48·2	21·3	69·5	
4·0	4·25	1 : 0·93	—	—	—	0·22	—	—	0·58	—	0·1973	—	7·9	7·9	after mixing.
—	—	—	—	—	—	0·36	—	—	1·11	—	0·3776	—	15·1	15·1	after passing CO_2 for 30 minutes.
—	—	—	—	—	—	0·42	—	—	1·18	—	—	—	—	—	after keeping in CO_2 for 1 day.
4·0	4·25	1 : 0·93	—	—	—	0·02	—	—	0·10	—	—	—	—	—	after passing air free from CO_2 for 1 hour.
4·0	4·25	1 : 0·93	—	—	—	0·04	—	—	0·10	—	—	—	—	—	after passing ordinary air for 1 hour.
4·0	4·25	1 : 0·93	—	—	—	nil	—	—	0·25	—	—	—	—	—	after boiling filtrate.
4·0	4·25	—	—	—	—	0·36	—	—	0·98	—	0·0370	—	1·6	1·6	2 per cent. mixtures.
4·0	4·5	—	—	—	—	0·20	—	—	1·22	—	0·1008	—	3·8	3·8	
4·0	5·0	—	—	—	—	0·12	—	—	2·04	—	0·5715	—	19·5	19·5	

of dissolved basic copper sulphate. From 4·25 to 7·38 grams the dissolved basic copper sulphate falls to a minimum. The sodium hydrogen carbonate rises regularly from nil, and beyond 7·38 grams of sodium carbonate free sodium carbonate appears.

Copper sulphate solution, as is well known, has an acid reaction, due to its tendency to form basic salts by hydrolysis. If the free

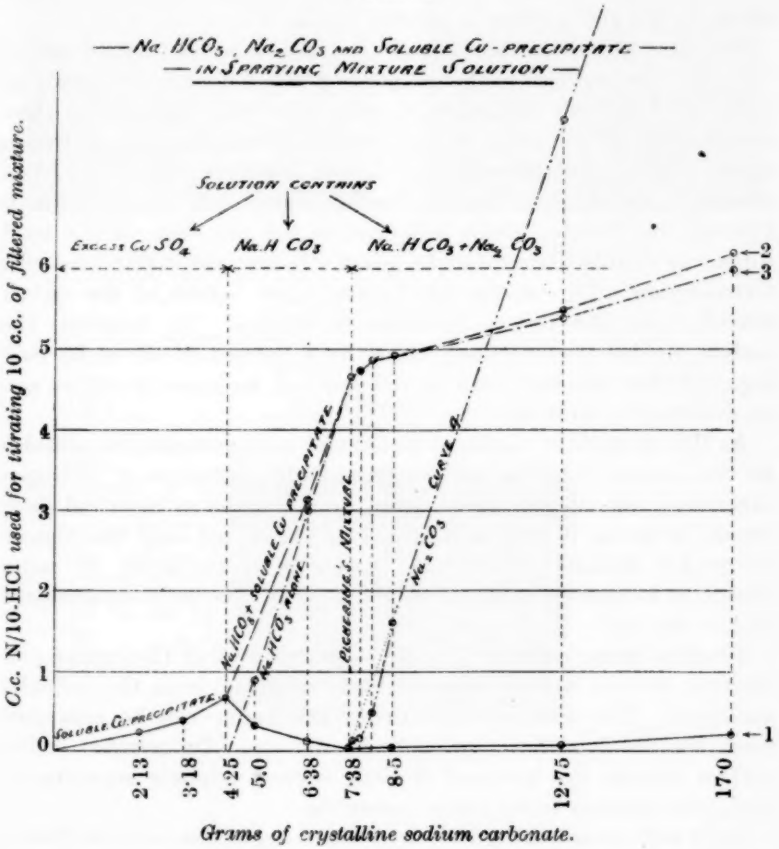
FIG. 1.



acid is neutralised by sodium carbonate, the solution will remain neutral or alkaline so long as the basic sulphate is kept in solution by the carbon dioxide evolved. With the gradual loss of the latter, the basic sulphate becomes insoluble, and further hydrolysis takes place until the solution is again acid. Further addition of sodium carbonate neutralises this acid, carbon dioxide is evolved, part of the

basic sulphate is precipitated, part of it is retained in solution by the carbon dioxide, and all these reactions are repeated until the whole of the copper sulphate is converted. The formation of basic copper sulphate is thus simply explained, and it is clear that a temporarily neutral solution can be obtained with very little sodium carbonate. A permanently neutral solution is obtained with 4·25

FIG. 2.



grams of sodium carbonate, which is less than the theoretical amount, because hydrolysis performs its share in the precipitation.

The sodium carbonate, besides neutralising the free acid, acts on the basic sulphate, converting it partly into basic carbonate. The carbon dioxide thus evolved increases the solubility of the basic sulphate, and with 4·25 grams of sodium carbonate the maximum

amount of free carbon dioxide and of dissolved basic sulphate is reached. Above 4·25 grams the excess of sodium carbonate is converted into hydrogen carbonate, the amount of carbon dioxide decreases, and proportionate amounts of basic sulphate are precipitated. At 7·38 grams of sodium carbonate all carbon dioxide has disappeared and the minimum of dissolved basic copper sulphate is reached. Above 7·38 grams the solution contains also normal carbonate, which forms soluble complex copper compounds, as is shown in the rising curve of soluble copper.

We have therefore established that the complete conversion of 4 grams of crystallised copper sulphate is effected with 4·25 grams of crystallised sodium carbonate, that is, 92·8 per cent. of the theoretical quantity. Such a mixture reacts neutral towards red litmus paper, faintly acid towards blue litmus (owing to the free carbon dioxide), and alkaline towards methyl-orange. If the mixture is filtered, the filtrate, which will contain 9·6 per cent. of the total copper as soluble basic sulphate, gives a heavy, red precipitate with ferrocyanide. This is due to the secondary action of the carbon dioxide, and the test is therefore misleading. If, however, the carbon dioxide is eliminated, either by a current of air or by boiling, and then the ferrocyanide test applied, no trace of copper can be detected in solution.

As this mixture of copper sulphate and sodium carbonate contains no free copper sulphate and no free alkali, carbonate or hydrogen carbonate, but, on the other hand, the maximum of dissolved basic copper sulphate, it may be regarded as having not only the highest fungicidal efficiency, but also a maximum potentiality to cause injury to foliage. This is borne out by Prof. Barker's experiments, and in the field.

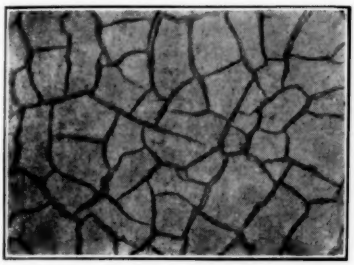
Physical examination of our mixture showed that the copper precipitate, as well as the dissolved basic sulphate, is in the colloidal condition. The sodium sulphate mother liquor can be separated from the dissolved basic sulphate by dialysis. On removal of the carbon dioxide the hydrosol of basic copper sulphate separates as well, the reaction being easily reversible.

As is well known, Burgundy mixture changes after a while from a colloidal into a crystalline condition, giving rise to a number of chemical reactions which will be examined hereafter.

The addition of 0·02 per cent. of glue was found to be most effective in prolonging the period during which the colloidal state exists.

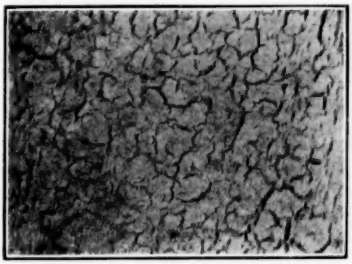
The three micro-photographs illustrate the drying of a colloidal film; (*a*) is without glue; (*b*) with glue; and (*c*) is without glue,

Colloidal
(A) *Without glue.*



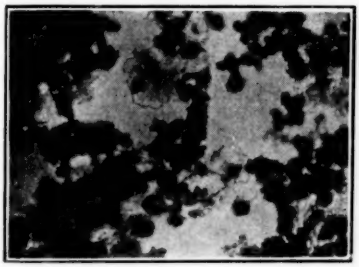
Magnified

Colloidal
(B) *With glue.*



Magnified.

Crystalline.
(C) *Without glue*



Magnified.

[*To face page* 914.

showing the change to the crystalline state. The separate crystals of malachite and sodium sulphate are clearly distinguishable.

(2) *The Reaction between Copper Sulphate and Sodium Hydrogen Carbonate.*

We found that the reaction between copper sulphate and sodium hydrogen carbonate proceeds similarly to the case of the normal carbonate; basic sulphate and basic carbonate are formed, carbon dioxide is set free, and a similar amount of basic sulphate is dissolved. The minimum weight of sodium hydrogen carbonate for complete conversion is 2·50 grams or 92·6 per cent. of the theoretical. This figure is close to the figure 92·8 found for the normal carbonate, and here also the hydrogen carbonate acts not as a direct precipitating agent, but as a neutralising agent. The copper precipitate obtained with the hydrogen carbonate has a paler blue colour, it separates out sooner from the mother liquor, being less hydrated, and contains Cu = 21·02; CO_2 = 5·67 per cent., and has a ratio CuO : CO_2 = 2·56 : 1.

(3) *Estimation of Carbon Dioxide in the Copper Precipitate, and of the Free Carbon Dioxide.*

TABLE II.

		Carbon dioxide evolved, per cent.	Percentage of carbon dioxide on total carbon dioxide. = 100 per cent.
Crystalline sodium carbonate plus sulphuric acid	on boiling	15·1	100
4 grams of $CuSO_4,5H_2O$ + 4·25 grams of crystalline sodium carbonate	15°	7·87	Average = 52·4
,, ,,	,,	7·95	
,, ,,	60°	9·78	64·8
,, ,,	on boiling	15·10	100·0

Table III.

Showing the Molecular Ratio $CuO:CO_2$ *in the Precipitate.*

No.	Mixture.	After..		Percentage in precipitate CuO.	Percentage in precipitate CO_2.	Mol. ratio. $CuO:CO_2$	
1	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$	½ hour.	colloid.	5·10	1·56	2·26 : 1	Filtered, not washed.
2	,,	1 day.	,,	6·10	1·85	2·28 : 1	
3	,,	1½ days.	,,	6·10	1·68	2·51 : 1	
4	,,	2 ,,	,,	6·10	1·53	2·76 : 1	
5	,,	½ hour.	,,	7·91	2·43	2·25 : 1	Filtered and washed twice.
6	,,	3 hours.	,,	7·91	2·32	2·36 : 1	
7	,,	4 days.	,,	7·91	2·26	2 42 : 1	
8	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$ and glue	1 hour	,,	7·67	2·42	2·19 : 1	Washed.
9	,,	36 days.	,,	6·76	1·35	3·46 : 1	,,
10	4 grams of $CuSO_4,5H_2O$ + 7·38 grams of $Na_2CO_3,10H_2O$	1 hour.	,,	7·54	2·36	2·21 : 1	,,
11	4 grams of $CuSO_4,5H_2O$ + 2·125 grams of $Na_2CO_3,10H_2O$	,,	,,	4·20	1·26	2·30 : 1	,,
12	4 grams of $CuSO_4,5H_2O$ + 1·0625 grams of $Na_2CO_3,10H_2O$	,,	,,	4·68	0·42	7·7 : 1	

TABLE III (*continued*).

Showing the Molecular Ratio $CuO:CO_2$ *in the Precipitate.*

No.	Mixture.	After.		Percentage in precipitate CuO.	Percentage in precipitate CO_2	Mol. ratio. $CuO:CO_2$	
13	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$ at 60°	1 hour	crystalline	—	—	2·93 : 1	
14	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$ at 80°	,,	,,	8·99	0·83	7·5 : 1	
15	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$ at 15°	7 days.	,,	31·89	7·51	2·94 : 1	
16	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$	4 ,,	,,	15·96	2·88	3·84 : 1	Sprayed on glass and dried.
17	,,	22 ,,	,,	47·89	8·38	3·97 : 1	
18	,,	8 ,,	,,	11·35	3·06	2·57 : 1	Filtered, washed, and stirred with water.
19	,,	7 ,,	,,	23·65	5·08	3·22 : 1	Passing air through for 2 hours. Left until crystalline.
20	,,	7 ,,	,,	19·53	3·79	3·56 : 1	As above, but air freed from CO_2.
21	,,	18 ,,	,,	33·5	11·9	1·95 : 1	In stoppered bottle.
22	,,	5 ,,	,,	23·8	8·39	1·99 : 1	Saturated CO_2.
23	,,	5 ,,	,,	27·3	9·46	2·00 : 1	,,
24	,,	1½ ,,	,,	24·58	4·14	4·11 : 1	Filtered, stirred with $NaHCO_3$ solution.
25	4 grams of $CuSO_4,5H_2O$ + 2·45 grams of $NaHCO_3$	1 hour.	colloid	21·02	5·67	2·56 : 1	

The average ratio in a 4·25 mixture is $CuO : CO_2 = 2·25 : 1$. Experiments 1 to 7 show that the copper precipitate, when formed, quickly loses carbon dioxide, the ratio altering gradually. On keeping the mixture in an open vessel, carbon dioxide is liberated by the decomposition of the basic copper carbonate and the precipitate becomes crystalline. It is not yet evident, however, from these experiments that the change of the colloidal to the crystalline state is due to any alteration of the ratio $CuO : CO_2$.

Fresh colloidal mixtures have the ratio $CuO : CO_2 = 2·26 : 1$.

Old crystalline mixtures have the ratio $CuO : CO_2 = 2·94 : 1$.

Old crystalline mixtures saturated with carbon dioxide $= 2·00 : 1$.

Old colloidal mixtures and glue have the ratio $CuO : CO_2 = 2·461$.

(4) *The Solvent Action of Carbonic Acid.*

An examination of the constitution of the dissolved basic copper compound present in acid, neutral, and alkaline mixtures has proved to us that only basic copper sulphate is dissolved by the carbon dioxide. Reference to curve 1 in Fig. 2 shows that the amount of copper precipitate dissolved by carbon dioxide rises gradually to a maximum containing 4·25 grams of sodium carbonate, then falls to its lowest point at 7·38. This maximum of dissolved copper corresponds with 9·6 per cent. of the total copper and is equal to 0·24 gram of copper per litre in a 1 per cent. mixture. By saturat-

TABLE IV.

Time.	Mixture 1 without glue. Soluble copper per litre. Gram.	Mixture 2 with glue. Soluble copper per litre. Gram.
After mixing	0·26	0·30
1 hour	—	0·22
2 hours	0·22	—
4 „	0·22	—
1 day	0·22	0·22
2 days	0·22	—
3 „	0·22	—
5 „	0·16	—
6 „	—	0·16
7 „	0·10 (precipitate begins to change)	—
9 „	0·06	0·10
10 „	0·06	—
11 „	0·06	0·10
13 „	0·02	0·10
14 „	0·00	—
16 „	—	0·06
20 „	—	0·02
22 „	—	0·01
24 „	—	nil

ing such a mixture with carbon dioxide the amount of soluble copper can be raised to 0·36 gram per litre. On the other hand, a mixture of 4 grams of crystallised copper sulphate and 8·5 grams of crystallised sodium carbonate containing 0·04 gram of copper per litre on being saturated with carbon dioxide shows scarcely any more soluble copper (0·06 gram per litre). The amount of basic copper sulphate in such a mixture being very small, the carbon dioxide finds little to dissolve, thus affording further proof that the copper carbonate is not dissolved by the carbon dioxide.

If an ordinary mixture, containing 4·25 grams of crystalline sodium carbonate, is allowed to remain in an open vessel, carbon dioxide is gradually evolved, and the amount of dissolved basic copper sulphate decreases in proportion. Table IV (p. 918) illustrates this.

After fourteen days an ordinary mixture containing 4·25 grams of crystalline sodium carbonate shows no more soluble copper and the precipitate has all turned to malachite. A similar mixture with 0·02 per cent. of glue loses its soluble copper more slowly, and after twenty-four days is still blue and colloidal.

(5) *The Basic Sulphate in the Copper Precipitate.*

TABLE V.

Mixture.		Sulphur in precipitate on total sulphur in mixture, = 100 per cent.	Copper precipitated. Per cent.	Molecular ratio, $CuO : SO_3$,
$CuSO_4$, $5H_2O$	Na_2CO_3, $10H_2O$.			
4	0·2688	2·10	6·25	2·8 : 1
4	0·5375	3·7	12·5	3·2 : 1
4	1·075	6·9	25·0	3·5 : 1
4	2·15	14·7	50·0	3·2 : 1
4	3·2256	22·4	75·0	3·3 : 1
4	3·7632	21·5	87·5	4·0 : 1
4	4·0320	17·1	93·75	5·3 : 1
4	4·30	6·3	100·0	15·0 : 1
4	5·375	4·3	100·0	22·4 . 1
4	6·45	3·2	100·0	30·9 : 1
4	8·60	0·75	100·0	126·0 : 1
4	4·30	10·10	100·0	9·6 : 1 (precipitated at 80°)

Basic sulphate is found in every mixture. With small amounts of sodium carbonate, more basic sulphate is found than basic carbonate. With an increasing amount of sodium carbonate the ratio $CuO : SO_3$ keeps fairly constant for a time. The ratio in our mixture is 15 : 1. Whereas the ratio $CuO : CO_2$ shows little difference in varying mixtures, the ratio $CuO : SO_3$ alters greatly in mixtures containing an excessive amount of sodium carbonate, and the SO_3

disappears almost completely in a mixture containing 8·6 grams of sodium carbonate.

Treatment with saturated aqueous carbon dioxide decreases the SO_3 in the precipitate, and sodium hydrogen carbonate dissolves the SO_3 completely.

The ratio $CuO : SO_3$ in the soluble basic copper sulphate was found to be 3·5 : 1.

(6) *Estimation of the Absorbed Sodium Carbonate in the Copper Precipitate.*

On examining the titration figures in table I it will be noticed that the amount of sodium carbonate and hydrogen carbonate found in solution of the mixtures with an excessive amount of sodium carbonate ranges from 4·5 to 7·8 per cent. below the amount calculated. This can only be accounted for by its being absorbed by the precipitate. A direct estimation of the alkali in the precipitate was made and the above figures were confirmed.

TABLE VI.

Mixture	Na_2CO_3 in precipitate on total soda used, =100 per cent.	Mol. ratio $CuO : Na_2CO_3$ in precipitate.
4 grams of $CuSO_4.5H_2O$ + 4·25 grams of $Na_2CO_3.10H_2O$ ...	4·0	73·5 : 1
4 grams of $CuSO_4.5H_2O$ + 4·25 grams of $Na_2CO_3.10H_2O$ with glue	4·1	75·3 : 1
4 grams of $CuSO_4.5H_2O$ + 8·5 grams of $Na_2CO_3.10H_2O$ ...	6·8	44·4 : 1

(7) *Causes of the Change from the Colloid to Malachite.*

Our experiments suggest that the colloidal state of the precipitate is dependent on the presence therein of sodium carbonate. The absorbed alkali is given up after some time and passes into solution, wherein it can be titrated.* The presence of an excessive amount of sodium carbonate in solution prevents this; a copper precipitate washed completely and stirred with sodium carbonate solution maintains its colloidal state indefinitely.

For the same reasons spraying mixtures with free sodium carbonate in solution (mixtures with more than 7·38 grams of sodium carbonate) retain the colloidal condition. Glue seems to act in a similar protective way.

Free carbon dioxide and sodium hydrogen carbonate destroy the

* When the maximum amount of free alkali in solution is reached, the change of the colloidal precipitate to the crystalline begins to be visible.

colloidal compound, the former acting on the absorbed sodium carbonate, forming hydrogen carbonate, the latter acting on the SO_3-groups, thus decomposing the compound.

A mixture containing 4·25 grams of crystallised sodium carbonate kept in an open vessel at 15° changes to malachite in seven days. Acid mixtures with less sodium carbonate or alkaline mixtures with less than 7·38 grams of sodium carbonate change sooner.

The presence of glue in every case retards the change.

Conclusions.

(1) On mixing copper sulphate with sodium carbonate solution three distinct copper compounds are formed: (*a*) Insoluble hydrated basic copper carbonate, which forms the bulk of the precipitate; (*b*) insoluble hydrated basic copper sulphate; and (*c*) soluble basic copper sulphate. Complete conversion of copper sulphate into these salts is obtained when for 1 molecule of copper sulphate 0·93 molecule of sodium carbonate is added, or for 4 grams of crystallised copper sulphate, 4·25 grams of crystallised sodium carbonate ($Na_2CO_3,10H_2O$).

(2) Judging by the results obtained, there appears to be no well-defined compound of copper, the composition altering according to conditions of precipitation. All the copper compounds are subject to rapid changes, the basic copper carbonate losing carbon dioxide and the dissolved basic copper sulphate soon becoming insoluble.

(3) A 1 per cent. mixture of 4 grams of copper sulphate and 4·25 grams of crystallised sodium carbonate made at 15° gives

(*a*) Basic copper carbonate containing CuO and CO_2 in the ratio 2·2 : 1.

(*b*) Insoluble basic copper sulphate containing CuO and SO_3 in the ratio 15 : 1.

(*c*) Soluble basic copper sulphate equal to 9·6 per cent. of the total copper present.

(4) On making the mixture at 15° free carbon dioxide is evolved, equal to 52·4 per cent. of the total carbon dioxide present in the sodium carbonate.

(5) At a higher temperature more carbon dioxide is evolved, until on reaching boiling point all carbon dioxide is expelled and the copper precipitate is converted into black copper hydroxide.

(6) The amount of basic copper sulphate formed is dependent on the amount of sodium carbonate used, and decreases as the latter is increased.

(7) The free carbon dioxide acts as a solvent on the basic copper sulphate only, not on the basic copper carbonate.

(8) The maximum of soluble basic copper sulphate is obtained in a mixture of 4 grams of copper sulphate and 4·45 grams of crystallised sodium carbonate for the reason that this mixture gives the maximum of free carbon dioxide.

(9) With larger amounts of sodium carbonate free carbon dioxide is neutralised to form sodium hydrogen carbonate.

(10) A mixture with 7·38 grams of crystallised sodium carbonate contains no more free carbon dioxide, and therefore a minimum of soluble basic copper sulphate.

(11) The copper precipitate at 15° contains absorbed sodium carbonate in the ratio $CuO : Na_2CO_3 = 74 : 1$.

(12) The whole of the copper precipitate is at first colloidal. After a short or long period, according to the temperature and the ratio of the ingredients in the mixture, the gel changes to the crystalline state.

(13) Addition of 0·02 per cent. of glue prolongs the life of the gel.

(14) Presence of free copper sulphate, or sodium hydrogen carbonate, or carbonic acid in the mixture accelerates the change of the colloidal to the crystalline state, whereas normal sodium carbonate helps to maintain the colloidal condition.

(15) The dissolved basic copper sulphate is in the form of hydrosol.

(16) The colloidal state of the precipitate appears to be conditional on the absorbed sodium carbonate.

(17) This absorbed sodium carbonate is found in the solution after some time, whereupon the change of the colloid to the crystalline begins to be visible.

(18) Changes in the sulphur content of the copper precipitate also take place during the change of the colloid to the crystalloid.

(19) The crystalline precipitate contains less carbon dioxide than the colloid. The ratio of $CuO : CO_2$ in old crystalline precipitate is found to be 2·94 : 1.

From the results obtained in this research it is apparent that the chemistry of "Bungundy mixture" is of a much more complex nature than previously suspected, and there are a number of questions which have to be further elucidated. The nature of the colloid solution and the conditions of its formation and change to the crystalline state await further investigations, and the influence produced by small quantities of glue indicates the importance of making further experiments with similar colloids.

Mond Nickel Co. Research Laboratory.

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LXXVIII.—*Examination of the Bark of* Croton gubouga. *Isolation of* 4-*Hydroxyhygric Acid*.

By John Augustus Goodson and Hubert William Bentley Clewer.

Croton gubouga, S. Moore, is a small tree growing on the low veldt in the Eastern Transvaal near the Sabi and Selati rivers. The bark of the tree has a considerable local reputation among the natives as a remedy for malaria, and both the seeds and the bark have been used by Captain Maberley in conjunction with opium in the treatment of malarial fever (*Lancet*, 1899, **157**, 874).

A preliminary examination of the bark and the seeds has been made by Mr. H. H. Green, B.Sc., in South Africa (private communication), who found that the ground bark caused purgation and emesis in dogs, but that rabbits were less sensitive to its action, although in doses of 1 gram per kilogram of body-weight it induced diarrhœa. In human beings administration of the bark according to Mr. Green causes an intense burning sensation in the throat, salivation, and slight nausea, with, in some cases, a slight laxative effect. The seeds exert a similar action. Mr. Green further observed that the acrid substance to which these effects are ascribed is extracted to some extent by hot water, and readily by ether.

The bark has also been examined by Greenish (*Pharm. J.*, 1918, **101**, 289), who found that the acrid constituent was largely extracted by hot light petroleum as well as by ether, chloroform, or alcohol.

For the material used in the present investigation the authors are indebted to Mr. I. B. Pole Evans, Chief of the Division of Botany, Union of South Africa.

The bark had a slight but not unpleasant odour. Dust from the ground bark caused sneezing and produced a burning sensation in the throat and on the tongue. It has not been possible to isolate the acrid constituent to which the irritant properties of the bark are due, in a form suitable for investigation, and it is possible that the seeds, which it is hoped to examine shortly, may prove more suitable for this purpose. The present paper deals chiefly with an acid isolated from the bark, which has proved to be a new optically active hydroxyhygric acid.

Preliminary Examination.

When extracted with Prollius' fluid the ground bark yielded a trace of alkaloid and furnished the following percentages of extract when exhausted in a Soxhlet apparatus with solvents in the order named: petroleum (b. p. 35—60°), 3; ether, 0·7; chloroform, 0·3; ethyl acetate, 0·8; alcohol, 4·3; total, 9·1.

Petroleum Extract.—This extract, on treatment with ether, left only a trace of insoluble matter. The solution yielded only traces of material to aqueous solutions of ammonium and potassium carbonates, but potassium hydroxide solution extracted a quantity of brown potassium salt, from which fatty acids (*A*), equivalent to 21 per cent. of the original extract, were recovered.

The solution left after the removal of the fatty acids contains the acrid constituent of the bark, but the authors have not yet been able to isolate this in a condition suitable for investigation (compare Greenish, *loc. cit.*). Hydrolysis, by alkalis, as described below, destroyed this acrid constituent.

The neutral material was hydrolysed by boiling for one hour with potassium hydroxide in alcoholic solution, after which the solution was concentrated, mixed with water, and extracted with ether to remove unsaponifiable matter. This, amounting to 20 per cent. of the original extract, included only a trace of hydrocarbon, or higher aliphatic alcohol, and consisted of semi-solid matter, from which a phytosterol was isolated, which gave a well-marked Liebermann reaction and on acetylation yielded a substance melting at 117°, probably a mixture of acetyl derivatives.

The remaining alkaline liquid was acidified with sulphuric acid, and the mixture distilled in a current of steam, when a yield of about 3·4 per cent. of volatile acids was obtained. The distillate was dissolved in an excess of barium hydroxide solution, the excess of baryta removed by carbon dioxide, and the filtrate concentrated. On adding silver nitrate solution to this liquid, silver was immediately precipitated; moreover, the solution instantly decolorised permanganate, indicating the presence of formic acid. On further concentration a quantity of a sparingly soluble barium salt separated. This was removed and converted into the acid, which was then dissolved in a slight excess of sodium hydroxide, and a silver salt prepared:

0·0413 gave 0·0178 Ag. Ag = 43·1.

$C_8H_{15}O_2Ag$ (silver *n*-octoate) requires Ag = 43·0 per cent.

The aqueous solution of the barium salts from which the above-described acid was separated still contained formic acid, and in

order to remove it, the solution was acidified, shaken with ether, and the ethereal solution well washed with water. In this way a further quantity of acid was obtained, which was fractionally converted into silver salts and the five fractions obtained were analysed:

1. 0·1315 gave 0·0665 Ag. Ag = 50·6.
2. 0·1817 „ 0·0934 Ag. Ag = 51·4.
3. 0·1448 „ 0·0744 Ag. Ag = 51·4.
4. 0·0951 „ 0·0490 Ag. Ag = 51·5.
5. 0·0273 „ 0·0141 Ag. Ag = 51·7.

$C_5H_9O_2Ag$ (silver valerate) requires Ag = 51·6 per cent.

The volatile acids present in the plant appear, therefore, to include formic, valeric, and *n*-octoic acids.

The acid liquid which had been distilled in a current of steam was extracted with ether, and the dark-coloured residue digested twice with petroleum. This left undissolved a dark-coloured, amorphous, resinous substance. The solution when concentrated gave a 23 per cent. yield of fatty acids, which were mixed with the 21 per cent. of free acids (*A*) previously obtained (see above). The acids were converted into lead salts, which from their behaviour appeared to be a mixture of lead salts of saturated and unsaturated fatty acids.

Ethereal Extract.—This consisted of a dark green resin, which on digestion with ether left a quantity of a light coloured substance undissolved. This was almost insoluble in the usual organic solvents except pyridine, from a dilute solution in which it separated in microscopic crystals melting at about 250° and giving the Liebermann reaction, whence it appeared to be a phytosterolin. The ethereal solution was then extracted first with water, removing about 10 per cent. of the extract, and finally with potassium hydroxide solution, which extracted 36 per cent. of acidic resin, leaving neutral resin; none of these yielded any crystalline material.

Chloroform and Ethyl Acetate Extracts.—These extracts consisted of amorphous resins. From the chloroform extract there separated gradually a fawn-coloured material, which was not obtained crystalline, nor could a crystalline acetyl derivative be prepared from it.

Alcoholic Extract.—This extract was redissolved in alcohol and water added, which precipitated a quantity of a nearly black tar. The clear liquid was treated with an excess of basic lead acetate, the precipitate filtered off, and the lead removed from the precipitate and filtrate by means of hydrogen sulphide in the usual way. The concentrated liquid from the former gave a nearly black colour with

ferric chloride and contained tannin. The concentrated filtrate was evaporated to complete dryness, and finally digested on the water-bath with nine successive portions of about 50 c.c. each of absolute alcohol to separate the large quantity of reducing sugars present. Each fraction was poured from the syrupy residue while hot, and when cold, again poured from a small amount of separated syrup, which was returned to the larger bulk. Crystals separated from each fraction when kept, but only a small quantity from the last. The whole amount of crystalline matter accumulated weighed about 6 grams. This substance proved to be *4-hydroxyhygric acid*, an optically active acid not previously described.

Examination of the Acid.

To obtain sufficient material for the identification of the acid, further quantities of the bark were extracted, when the following varying percentage yields were obtained: 0·41, 0·21, and 0·25, amounting in all to 16·35 grams of crude acid.

The product may be readily purified by boiling its solution in water with animal charcoal, repeatedly concentrating the filtrate under diminished pressure with additions of alcohol, until the pure acid separates from the hot solution in colourless needles or prisms, which contain varying amounts of water of crystallisation, thus:

I. 0·1986 lost 0·0170 at 110°. $H_2O = 8·56$.
II. 0·2108 ,, 0·0108 ,, 110°. $H_2O = 5·13$.

Although the acid is very readily soluble in water it may be crystallised from that solvent. 7·05 Grams of substance were dissolved in water, and the solution was concentrated until about 4·5 grams of water remained. The solution was seeded and allowed to remain overnight, when 1·25 grams of the acid had separated in crystals, which appeared to be truncated prisms. These crystals, after being dried in the air, were found to contain one molecule of water:

0·2035 lost 0·0220 at 110°. $H_2O = 10·8$.

$C_6H_{11}O_3N,H_2O$ requires $H_2O = 11·0$ per cent.

I. 0·1324 * gave 0·2402 CO_2 and 0·0938 H_2O. $C = 49·5$; $H = 7·9$.
II. 0·1090 * ,, 0·1976 CO_2 ,, 0·0778 H_2O. $C = 49·5$; $H = 8·0$.
0·1474 gave 12·6 c.c. N_2 at 17° and 746 mm. $N = 9·7$.

$C_6H_{11}O_3N$ requires $C = 49·6$; $H = 7·6$; $N = 9·7$ per cent.

Methoxyl estimation: 0·1751 gave no AgI. $MeO = 0$.

N-*Methyl estimation:* 0·1751 ,, 0·2430 AgI. $NMe = 17·2$.

$C_5H_8O_3N·CH_3$ requires $NMe = 20·0$ per cent.

* Dried at 105°.

The acid decomposes with effervescence at 242°, possesses little if any taste, is acid to litmus, but cannot be titrated, is not hygroscopic, and is optically active.

The specific rotatory power was determined in water of (*a*) a specimen of the acid crystallised from alcohol and containing $H_2O = 5{\cdot}13$, and (*b*) a specimen crystallised from water and containing $H_2O = 10{\cdot}8$ per cent.:

(*a*) $c = 4{\cdot}9910$, $l = 1$-dcm., $\alpha_D - 4{\cdot}02°$; $[\alpha]_D - 80{\cdot}5°$ or $[\alpha]_D - 84{\cdot}9°$ for the anhydrous substance.

(*b*) $c = 5{\cdot}2300$, $l = 1$-dcm., $\alpha_D - 3{\cdot}98°$; $[\alpha]_D - 76{\cdot}2°$ or $[\alpha]_D - 85{\cdot}4°$ for the anhydrous substance.

It gives a strong pyrrole reaction, and dissolves copper oxide with the formation of a copper salt. A quantity (0·2 gram) of the substance was dissolved in water, and the solution boiled for several hours with an excess of powdered copper oxide, the excess of copper oxide filtered off, and the filtrate concentrated. Blue prisms separated, which were dried on a porous tile, washed with 70 per cent. alcohol, and dried in the air:

0·1021 lost 0·0200 at 110°. $H_2O = 19{\cdot}6$.

$C_{12}H_{20}O_6N_2Cu,4H_2O$ requires $H_2O = 17{\cdot}0$; $C_{12}H_{20}O_6N_2Cu,5H_2O$ requires $H_2O = 20{\cdot}4$.

0·0669 (anhydrous salt) gave 0·0146 CuO. $Cu = 17{\cdot}4$.

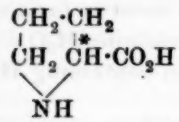
$C_{12}H_{20}O_6N_2Cu$ requires $Cu = 18{\cdot}1$ per cent.

Constitution of the Acid from Croton gubouga *Bark.*

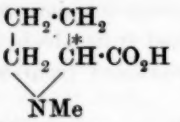
The evidence already given indicates that the substance is a 4-hydroxy-1-methylpyrrolidine-2-carboxylic acid (4-hydroxyhygric acid). Two such compounds have been synthesised by Leuchs and Felser (*Ber.*, 1908, **41**, 1726), namely, two optically inactive forms of 4-hydroxy-1-methylpyrrolidine-2-carboxylic acid. A comparison of the principal properties of these acids with that from *C. gubouga* bark is given in the following table:

	Formula.	$[\alpha]_D$.	M. p.	Reaction.	Taste.
Acid from Croton bark	$C_6H_{11}O_3N$	−85·4°	242°	faintly acid.	little or no taste.
a-4-Hydroxy-1-methylpyrrolidine-2-carboxylic acid.....	$C_6H_{11}O_3N$	inactive.	207–208°	neutral.	marked sweet taste
b-4-Hydroxy-1-methylpyrrolidine-2-carboxylic acid	$C_6H_{11}O_3N$	inactive.	226–227°	faintly acid.	sweetish insipid taste.

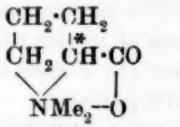
Comparison of the specific rotations of the closely related pyrrolidine derivatives indicates that in all probability this acid from Croton bark is 4-hydroxyhygric acid (γ-hydroxy-*N*-methylproline):



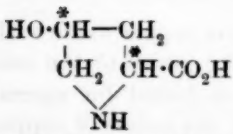
l-Proline (natural) (Fischer), $[\alpha]_D$ −77·4°.



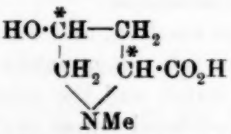
Hygric acid; active form does not appear to have been isolated.



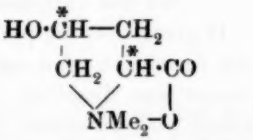
l-Stachydrine (natural), $[\alpha]_D$ of hydrochloride −26·5° (Yoshimura and Trier).



l-Hydroxyproline (Fischer), $[\alpha]_D$ −81·1° (natural) (Leuchs and Brewster), $[\alpha]_D$ −76·3° (synthetic).



Formula suggested for acid from Croton bark, $[\alpha]_D$ −85·4° (natural).



Betonicine hydrochloride, $[\alpha]_D$ −24·79° (natural); hydrochloride, $[\alpha]_D$ −24·1° (synthetic).

Turicine (natural), hydrochloride $[\alpha]_D$ +24·65°.

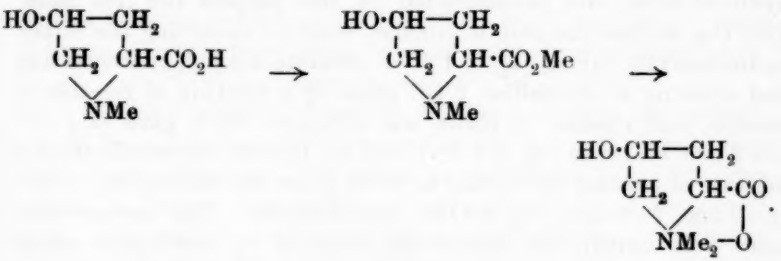
(Küng and Trier).

Leuchs and Brewster (*Ber.*, 1913, **46**, 986) have synthesised *l*-hydroxyproline, and Küng (*Zeitsch. physiol. Chem.*, 1913, **85**, 217) on methylating this substance obtained a mixture of the betaines, betonicine and turicine. If, therefore, the acid from *Croton gubouga* bark is in reality 4-hydroxyhygric acid it should in like manner, on methylation, give betonicine and turicine. Küng's method of methylation, with slight modification, was adopted, and resulted in the production of a mixture of betonicine and turicine, thus proving the acid to be 4-hydroxyhygric acid.

Küng (*loc. cit.*) has pointed out that turicine and betonicine are not enantiomorphs. When *l*-hydroxyproline or *l*-hydroxyhygric acid is methylated, using methyl iodide and alkali, it is probable that racemisation occurs and that one of the carbon atoms only, namely, that attached to the carboxyl group, is concerned in the racemisation. It will be interesting to see whether optically active hygric acid, which so far does not appear to have been obtained, and will only possess one asymmetric carbon atom, will yield on methylation two stereoisomeric betaines.

It seemed possible that methylation of the hydroxyhygric acid might be accomplished without racemisation if the use of alkali were avoided, and so evidence might be secured as to which of the

betaines, betonicine or turicine, corresponds with *l*-hydroxyproline and 4-hydroxyhygric acid. It was hoped that by passing hydrogen chloride into boiling methyl alcohol containing 4-hydroxyhygric acid the methyl ester would first be formed, and would pass into the corresponding betaine, thus:



It is probable that the ester was formed, but was rapidly hydrolysed, since on treating the hydrochloride with silver oxide the original 4-hydroxyhygric acid was recovered unchanged.

Methylation of the Acid.

A preliminary experiment was carried out, using 1 gram of the acid, which was dissolved in a mixture of 2 c.c. of water and 20 c.c. of methyl alcohol. Five c.c. of a solution of 6 grams of potassium hydroxide in 100 c.c. of methyl alcohol, and a like quantity of a solution of methyl iodide in methyl alcohol (3 grams in 20 c.c.), were added alternately 1 c.c. at a time. As the solution remained alkaline, a further 5 c.c. of the methyl iodide solution were added, and the mixture boiled on a water-bath for half an hour. One c.c. of methyl iodide was then added and sufficient methyl-alcoholic potassium hydroxide to render the liquid alkaline. The solution was boiled for about twenty minutes and made alkaline, again boiled for five minutes and made alkaline, and the operation repeated until the alkalinity persisted. The alcohol was distilled off, the residue dissolved in water, the solution made slightly acid with hydrochloric acid, and boiled with excess of silver chloride. The silver iodide and excess of silver chloride were filtered off, and the filtrate evaporated to dryness under diminished pressure. The residue was treated with absolute alcohol and again evaporated to dryness. The dry residue was extracted with five small quantities of boiling absolute alcohol; the first three of which removed all but traces of the hydrochlorides of the betaines. The alcohol was distilled off and the rotation of the residue determined, using water as solvent ($c = 6{\cdot}4275$, $l = 1$-dcm., $\alpha_D + 0{\cdot}075°$; $[\alpha]_D + 1{\cdot}2°$).

This result indicated that the methylation had proceeded as expected, and that a mixture of turicine and betonicine hydrochlorides in about equal amounts had been produced.

Küng and Trier (*loc. cit.*) pointed out the difficulty of separating turicine and betonicine by fractional crystallisation of their hydrochlorides, and recommended for this purpose the free bases. This the authors are able to confirm, since on dissolving the mixed hydrochlorides having $[\alpha]_D$ +1·2° in absolute alcohol, concentrating and allowing to crystallise, 0·667 gram of a mixture of rosettes of needles, and rosettes of plates was obtained which gave $[\alpha]_D$ +3° (c=3·335, l=1-dcm., α_D +0·10°), and on further recrystallisation a mixture of crystals amounting to 0·456 gram and having $[\alpha]_D$ +5·0° (c=2·280, l=1-dcm., α_D 0·115°) was obtained. The various solutions were united, the alcohol was removed by distillation under diminished pressure, and the free bases were liberated by treating the aqueous solution with excess of silver oxide. The silver chloride and excess of silver oxide were filtered off, the filtrate was concentrated, absolute alcohol added, and the solution again concentrated, this operation being repeated until crystals separated out on cooling. 0·137 Gram of substance crystallised in long prisms, which had a sweet taste, decomposed at 250° with frothing, and gave $[\alpha]_D$ +21·2° (c=2·6400, l=1-dcm., α_D +0·58°).

Five grams of the acid were then methylated as described above with slight modifications. The same proportions of methyl iodide, methyl-alcoholic potassium hydroxide and acid were used, but the solutions were more concentrated. The alcoholic solution of the mixed hydrochlorides from the extraction of the dried mixture of potassium chloride and betaine hydrochlorides was kept overnight to separate as much potassium chloride as possible. When the hydrochlorides had been converted into bases by treating their aqueous solution with silver oxide and the silver chloride and undissolved excess of silver oxide removed by filtration, hydrogen sulphide was passed through the solution of the bases to remove any silver in solution. The solution of the betaines was concentrated to low bulk under diminished pressure, alcohol added, and the solution again concentrated; this operation was repeated until crystallisation set in on cooling. From the mother liquor two further crops were obtained on concentration.

Crop I consisted of nearly pure turicine, amounting to 1·7 grams. The air-dried substance was examined polarimetrically in water:

$$c=2·5330,\ l=1\text{-dcm.},\ \alpha_D +0·87°;\ [\alpha]_D +34·3°.$$

On recrystallisation until the optical rotation was constant, the value $[\alpha]_D$ +40·9° was obtained for the anhydrous substance.

Crop II weighed 1·2 grams and was a mixture:

$c=2·5840$, $l=1$-dcm., α_D $-0·48°$; $[\alpha]_D$ $-18·6°$.

Crop III, weighing 1·06 grams, was also a mixture:

$c=2·6180$, $l=1$-dcm., α_D $-0·41°$; $[\alpha]_D$ $-15·7°$.

Crops II and III were united, converted into hydrochlorides, dissolved in absolute alcohol, and the solution was concentrated, when 1·45 grams of nearly pure betonicine hydrochloride crystallised out:

$c=3·3765$, $l=1$-dcm., α_D $-0·75°$; $[\alpha]_D$ $-22·2°$.

As it was found difficult to remove all traces of potassium chloride from the betonicine hydrochloride, and it was not possible to obtain a higher value than $[\alpha]_D$ $-22·9°$ on recrystallising this particular specimen, a further methylation of the acid was tried with good results, using sodium hydroxide instead of potassium hydroxide; with this difference, 3·9 grams of the acid were methylated as in the previous experiment; 1·2731 grams of crude turicine were obtained as a first crop:

$c=6·3655$, $l=1$-dcm., α_D $+2·25°$; $[\alpha]_D$ $+35·3°$ for the anhydrous substance.

The bases in the mother liquor were converted into hydrochlorides, and crystallised from absolute alcohol; 1·322 grams of nearly pure betonicine hydrochloride were obtained, having $[\alpha]_D$ $-22·7°$ ($c=6·6100$, $l=1$-dcm., α_D $-1·50°$). This was recrystallised until its optical rotation remained constant, the highest reading being $[\alpha]_D$ $-24·8°$ ($c=3·5900$, $l=1$-dcm., α_D $-0·89°$).

The bases in the mother liquor from the betonicine hydrochloride ($[\alpha]_D$ $-22·7°$) were regenerated by treatment with silver oxide. On crystallisation from alcohol a further 0·4012 gram having $[\alpha]_D$ $+4·0°$ ($c=2·0060$, $l=1$-dcm., α_D $+0·08°$) was obtained.

The formation of a mixture of turicine and betonicine by the methylation of the acid from *Croton gubouga* bark leaves no doubt that the acid is 4-hydroxyhygric acid, as formulated on p. 928.

Properties of Turicine.

Turicine crystallises from alcohol in flat prisms containing one molecule of water of crystallisation, which it rapidly loses in a vacuum desiccator. It is neutral to litmus, is not hygroscopic, has a sweet taste, and gives an intense pyrrole reaction. The anhydrous substance decomposes with frothing at 260°, as did a specimen kindly supplied by Prof. A. Küng; the decomposition point was not depressed on mixing the two specimens. The hydrated substance commenced to melt at about 249°, but finally decomposed with frothing at 256°. Prof. Küng's specimen, and a mixture of the

two, behaved in the same way. (Found, $H_2O = 10{\cdot}59$; $C_7H_{13}O_3N,H_2O$ requires $H_2O = 10{\cdot}17$. Found, $C = 52{\cdot}7$; $H = 8{\cdot}3$. $C_7H_{13}O_3N$ requires $C = 52{\cdot}8$; $H = 8{\cdot}2$ per cent.)

The specific rotations of three specimens of the anhydrous substance were determined in water:

I. $c = 1{\cdot}8065$, $l = 1$-dcm., $\alpha_D + 0{\cdot}75°$; $[\alpha]_D + 41{\cdot}5°$.
II. $c = 1{\cdot}3950$, $l = 1$-dcm., $\alpha_D + 0{\cdot}57°$; $[\alpha]_D + 40{\cdot}9°$.
III. $c = 2{\cdot}0980$, $l = 1$-dcm., $\alpha_D + 0{\cdot}85°$; $[\alpha]_D + 40{\cdot}5°$.

Küng and Trier give $[\alpha]_D + 36{\cdot}26°$ for the hydrated betaine corresponding with $[\alpha]_D + 40{\cdot}4°$ for the anhydrous substance.

Turicine Hydrochloride.—This was prepared from the pure base. When crystallised rapidly from absolute alcohol it separated in needles, but when allowed to crystallise slowly, six-sided tablets were obtained. It is acid to litmus, and decomposes with frothing at 224°; Küng and Trier give 222° and 223° as the melting and decomposing point. Its specific rotation was determined in water. $c = 2{\cdot}8000$, $l = 1$-dcm., $\alpha_D + 0{\cdot}72°$; $[\alpha]_D + 25{\cdot}7°$. Küng and Trier give $[\alpha]_D + 24{\cdot}65°$, and state that turicine is not hygroscopic, but the authors are of the opinion that it is slightly hygroscopic.

Turicine aurichloride was obtained by adding gold chloride solution to a concentrated aqueous solution of turicine hydrochloride. The crystals, which separated rapidly, were collected, dissolved in hot water, and the solution was allowed to cool, when the double chloride crystallised in clusters of yellow prisms. The decomposition point was determined in the same bath with a specimen of turicine aurichloride kindly supplied by Prof. Küng, and a mixture of the two specimens; the decomposition with frothing occurred in each case at 230—232°. Küng and Trier give the melting and decomposing point as 232°. (Found, $Au = 39{\cdot}0$; $C_7H_{13}O_3N,HAuCl_4$ requires $Au = 39{\cdot}5$ per cent.)

Properties of Betonicine.

The free base was obtained from the pure hydrochloride by treating with silver oxide. It crystallises anhydrous from alcohol in short, four-sided, truncated pyramids, is more readily soluble in alcohol than turicine, has a sweet taste, is neutral to litmus, and gives an intense pyrrole reaction. Küng and Trier state that it is not hygroscopic, and that it melts and decomposes at 243—244°; the purest specimen obtained by the authors was slightly hygroscopic and decomposed with frothing at 252°. (Found, $C = 52{\cdot}7$; $H = 8{\cdot}5$. $C_7H_{13}O_3N$ requires $C = 52{\cdot}8$; $H = 8{\cdot}2$ per cent.) The specific rotation was determined in water:

$c = 3{\cdot}5050$, $l = 1$-dcm., $\alpha_D - 1{\cdot}23°$; $[\alpha]_D - 35{\cdot}1°$.

Küng and Trier give $[\alpha]_D$ −36·6°.

Betonicine hydrochloride crystallises from absolute alcohol in needles or prisms, which, after drying at 105°, decompose with frothing at 227°; a specimen supplied by Prof. Küng, which was slightly coloured, after drying at 105°, decomposed with frothing at 224°; a mixture of the two specimens decomposed at an intermediate temperature. Küng and Trier give the melting and decomposing point as 222—223°. The hydrochloride is not hygroscopic and is acid in reaction. The specific rotatory power was determined in water:

$c=3·5900$, $l=1$-dcm., α_D −0·89°; $[\alpha]_D$ −24·8°.

Küng and Trier give $[\alpha]_D$ −24·79° for natural betonicine hydrochloride, and Küng $[\alpha]_D$ −24·1° for his synthetic product.

Betonicine Aurichloride.—To a concentrated solution of betonicine hydrochloride a solution of gold chloride was added. There was no immediate separation of crystals as in the case of turicine hydrochloride. The solution was accordingly concentrated and, on cooling, four-sided, yellow plates crystallised out. When redissolved in hot water and kept, clusters of yellow tablets were obtained. The substance decomposed with frothing at 230—232°, the same temperature as a specimen supplied by Prof. Küng, and a mixture of the two specimens also decomposed at this point. (Found, Au = 39·2. $C_7H_{13}O_3N,HAuCl_4$ requires Au = 39·5 per cent.)

The authors desire to take this opportunity of thanking Prof. Küng for his kindness in supplying them with specimens of turicine, turicine aurichloride, betonicine hydrochloride, and betonicine aurichloride for comparison.

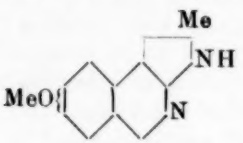
WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C. 1. [*Received, July 9th*, 1919.]

LXXIX.—*Harmine and Harmaline. Part III.*

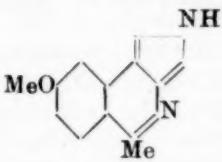
By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

IN 1912 the present authors, having located in the harmine molecule a methyl group similarly situated to that in quinaldine, suggested that the alkaloid contains a fused ring system comprising a benzene, pyrrole, and pyridine nucleus, and constructed a constitutional formula (T., **101**, 1775) which satisfied the requirements of the facts then known. This expression (I) was discarded by O. Fischer (*Ber.*, 1914, **47**, 99) in favour of the formula II on account of his

discovery that harminic acid* may be oxidised by nitric acid in a sealed tube with the formation of *iso*nicotinic acid (III), and this observation was held to be inconsistent with the assumption made in I that there is an imino-group attached to the pyridine ring:



(I.)



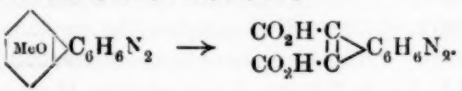
(II.)

As the result of a further examination of derivatives of harmine and harmaline we are now convinced that neither of these formulæ is correct, and, after a careful reconsideration of the whole subject, have deduced fresh expressions which it is believed are more satisfactory representations of the chemistry of these bases. The argument which has been developed may be presented in the following sections.

The Ring System of Harmine and its Derivatives.

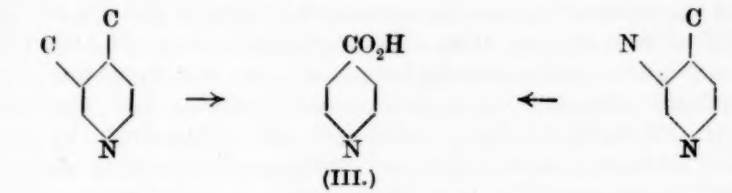
Harmine, $C_{13}H_{12}ON_2$, contains a methyl and a methoxyl group and may be written $C_{11}H_6N_2Me{\cdot}OMe$, and is therefore a derivative of a substance, $C_{11}H_8N_2$. Although the methoxyl and methyl groups have been separately eliminated with the production of compounds called harman and norharmine respectively, the parent, $C_{11}H_8N_2$, which might be called *norharman*, has not yet been prepared. Now harmaline, which is dihydroharmine, yields *m*-nitroanisic acid (IV) on oxidation with nitric acid (O. Fischer and Boesler, *Ber.*, 1912, **45**, 1934), whilst the production of *iso*nicotinic acid has already been referred to above. The existence of both benzene and pyridine nuclei in norharman is therefore certain, and, on inspection of the composition, it will be seen that there is no alternative to the theory that this substance must contain a benzene, pyridine, and pyrrole nucleus fused together as are the benzene nuclei in anthracene or phenanthrene. So much was already recognised, and in addition that the benzene nucleus occupies a terminal position in the system, a fact which follows from the consideration of the relation of harminic acid to harmine. It is neces-

* This acid is obtained from harmine by oxidation with chromic acid (O. Fischer and E. Tauber, *Ber.*, 1885, **18**, 403).

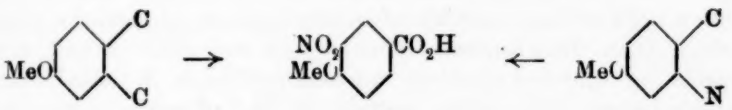


sary to recall these points in order to develop the present discussion.

When a compound containing a fused ring system is energetically oxidised, it is usual to be able to recognise, in the product, residual groups which are derived from the nucleus destroyed by the oxidation and are situated at both the points of fusion of the original rings. Yet, in the degradation of harmine, this rule is not followed in the two cases which have been already mentioned, namely, the production of nitroanisic acid from harmaline (or nitroharmaline) and that of *iso*nicotinic acid from harminic acid. In both these reactions one of the positions of ring fusion is represented by a hydrogen atom in the oxidation product. It will be necessary to assume the possibilities shown under *A* or *B* below, and these are clearly the only alternatives:



(III.)

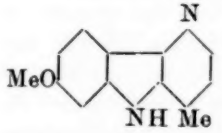


A. (IV.) *B.*

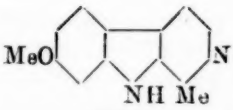
In attempting to make a choice from these alternatives, neither of which is quite in accord with previous experience, we have been guided by two main considerations. The first is that the conditions of elimination of carbon from direct union with aromatic nuclei are much better understood than those governing the similar removal of nitrogen, and whereas experimental and other evidence is not at present available to enable us to refute the alternative *B*, we are on much firmer ground in regard to *A*, which we consider is opposed to experience. O. Fischer suggested that a nitromethoxyphthalic acid is the intermediate product in the oxidation of harmaline, and that this loses carbon dioxide with the formation of nitroanisic acid. The supposed intermediate product does not, however, appear to have been isolated, and we can find no record in the literature of an analogous reaction in which a phthalic acid at all similarly constituted loses one of its carboxyl groups under comparable conditions. In the production of *iso*nicotinic acid scheme *A* makes it necessary to assume the elimination of carbon

attached to the β-position in a pyridine nucleus, whilst that in the γ-position remains in the form of a carboxyl group. When it is remembered that, of the three pyridinemonocarboxylic acids, it is only nicotinic acid which requires to be heated with soda-lime in order to convert it into pyridine, and, further, that quinolinic acid and cinchomeronic acid both yield nicotinic acid on being strongly heated, it will be realised how relatively firm is the attachment of carbon to the β-position. It is consequently very improbable from this point of view that a pyridine derivative convertible into *iso*nicotinic acid by a simple oxidation process can have a carbon atom attached to the β-position. The second argument in favour of the assumption that these degradations involve the elimination of nitrogen, and not of carbon, from direct combination with the surviving nuclei, is that we have obtained experimental indications that the benzene nucleus of a harmine derivative is actually directly attached to a nitrogen atom. Tetrahydroharmine, $C_{13}H_{16}ON_2$, condenses with diazobenzenesulphonic acid with the formation of a sparingly soluble, crystalline, orange-yellow azo-compound, $C_{13}H_{15}ON_2 \cdot N_2 \cdot C_6H_4 \cdot SO_3H$, which dyes silk yellow from an acid bath, behaves as an indicator, and undergoes changes with acid and alkali closely resembling those characteristic of methyl-orange. Comparison with a large number of azo-derivatives of various types derived from diazobenzenesulphonic acid and such second components as dihydroberberine, anhydrocryptopine, β-dialkylaminocrotonic esters, β-diketones, pyrrole, α- and β-methylindole and indole, showed that the change from yellow to crimson is exhibited only by the true benzeneazobenzene derivatives. It would therefore appear that tetrahydroharmine is an aniline derivative with a free para-position, and naturally the argument applies to all the bases of the group so far as it throws light on their nuclear structure. We are therefore compelled to accept this surprising elimination in a nitric acid oxidation of a side-chain commencing with a nitrogen atom, and in attempting to form an idea as to the possible mechanism of the reaction the clue seems to be given by the oxidation of phenylhydrazine with the production of benzene. Possibly, the imino-group of harmine becomes converted into the nitroamino- or nitrosoamino-group, and one of these becomes reduced by readily oxidisable groups produced in the course of the reaction, so that, at a certain stage, the condition is reached at which nitrogen is eliminated and hydrogen replaces the whole side-chain. Accepting scheme *B* and its implications, it is quite clear that if harmine contains no carbon attached to its pyridine nucleus in the β-position, this nucleus cannot be fused with a benzene ring and harmine cannot be a derivative of quinoline or *iso*quinoline. The order of

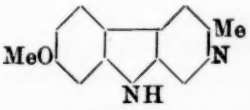
fusion of rings is, then, benzene–pyrrole–pyridine, and the methyl group must be in the pyridine nucleus. Further, the only possible formulæ for harmine, bearing in mind the formation of nitroanisic acid from harmaline, are the following:



(V.)

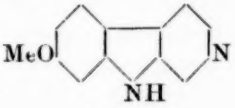


(VI.)



(VII.)

In V the methyl group is in the γ-position in the pyridine ring, and this is inconsistent with the behaviour of harmine, which, as we have already stated, closely resembles quinaldine in its reactions. It shows the quinophthalone reaction and condenses with benzaldehyde to benzylideneharmine, a styryl derivative, which may be oxidised to norharminecarboxylic acid (T., 1912, **101**, 1784). The latter gives a red coloration with ferrous sulphate, and easily loses carbon dioxide, on heating in glycerol, with the formation of norharmine. We therefore reject the structure V, and consider harmine must be either VI or VII, and since these differ only in the position attributed to the methyl group, the constitution of norharmine is determined and is shown in VIII:

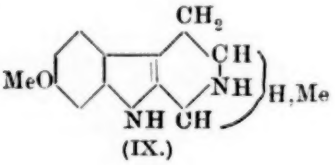


(VIII.)

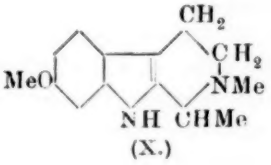
The Constitution of Harmine.

The decision between formulæ VI and VII for harmine is a difficult one, and cannot at present be made with precision, but there are strong indications which cause us to much prefer the former alternative. A glance at the structure of norharmine will show that it is a species of *iso*quinoline in which indole takes the place of benzene. Alkaloids of the *iso*quinoline group are known which contain a methyl group in their pyridine or reduced pyridine rings, and of these corydaline has been most completely investigated. The methyl group in VI is in the position which an analogy to corydaline would suggest. Further light is thrown on the problem by the study of the oxidation of *N*-methyltetrahydroharmine, and some preliminary remarks must be made in regard to the constitution of this substance. Harmine or harmaline, by reduction in acid or alkaline solution, yields the same tetrahydroharmine as the end-

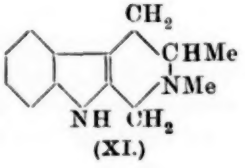
product, and up to the present no more highly hydrogenated derivative has been obtained. The reduction of metho-salts of harmaline produces a methyltetrahydroharmine, and this is the true *N*-methyl derivative of tetrahydroharmine because the latter is converted into the methyl hydrogen sulphate of the former by treatment with methyl sulphate (see p. 961). Evidently, the four hydrogen atoms which may be added to harmine and some of its derivatives always assume the same positions in the molecule, and this is clearly due to the hydrogenation of the pyridine nucleus leaving the indole nucleus intact. It is well known that indoles are exceedingly difficult to reduce, and the fact that harmine yields only a tetrahydro-derivative is to be regarded as evidence confirming our view of the nature of its fundamental structure. Tetrahydroharmine is shown in IX, and it is desirable at this stage to consider whether or no a substance of this constitution would couple with diazonium salts in the way which is so characteristic of this base (see p. 936). It might well be thought that a dialkylindole would not be reactive on account of the conjugation of the nitrogen in the indole ring, and for comparison we prepared a pure specimen of 2:3-dimethylindole by repeated treatment of the crude substance with *p*-dimethylaminobenzaldehyde in warm alcoholic hydrochloric acid solution. The product was quite free from ethylindole, and gave no pine-shaving reaction and no coloration with *p*-dimethylaminobenzaldehyde in aqueous-alcoholic hydrochloric acid solution. In dilute acetic acid it condensed with diazobenzenesulphonic acid with the production of an orange-red azo-compound. In the case of IX there is also a methoxyl group in the ortho-position to the point of entry of the azo-group, and this is a circumstance which is well known to facilitate the coupling and to enhance the halochromic phenomena of the product. Obviously formula IX represents a substance which should behave towards diazo-salts as tetrahydroharmine actually does:



(IX.)



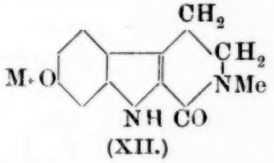
(X.)



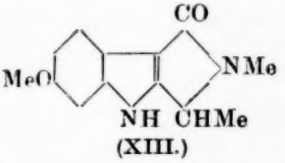
(XI.)

A curious analogy between tetrahydroharmine and 2:3-dimethylindole is shown by the colour reactions with *p*-dimethylaminobenzaldehyde and aqueous-alcoholic hydrochloric acid on heating. The dimethylindole slowly develops a pale blue colour, which fades to pale greenish-yellow on cooling the solution, and the alternation of colours on heating and cooling can be made as often as desired. Tetrahydroharmine behaves entirely similarly except that the hot liquid is bluish-pink and the cold solution yellow.

Returning to the question of the position of the methyl group in harmine, *N*-methyltetrahydroharmine will be X or XI according as harmine is taken as VI or VII respectively. On oxidation with potassium permanganate in acetone solution this base, $C_{14}H_{18}ON_2$, is partly converted into a neutral substance melting at 228°, which has the composition $C_{13}H_{14}O_2N_2$, and clearly the newly acquired oxygen atom forms part of a carbonyl group which by direct union with the basic nitrogen neutralises its salt-forming character. At the same time the oxidation has removed a carbon atom, most probably originally in the form of a methyl group. This substance (m. p. 228°) was recovered unchanged after heating at 100° with phosphorus pentachloride and phosphoryl chloride, although a clear solution was obtained. On the basis of formula XI for *N*-methyltetrahydroharmine, all possible structures for the oxidation product will contain either the grouping ·NH·CO· or ·CH_2·CO·, and in either case a reaction with phosphorus pentachloride would be anticipated. Assuming formula X, however, it is possible to construct two expressions (XII and XIII) for the compound (m. p. 228°), which are in harmony with its composition and other properties:

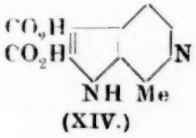


(XII.)

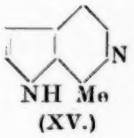


(XIII.)

The evidence, just mentioned, is not quite conclusive, since the apparent failure to react with phosphorus pentachloride may have been due to the ready hydrolysis of the chloro-derivative by water, but, so far as it goes, it favours formula VI for harmine, and we have therefore provisionally adopted this expression. It follows that harminic acid and *apo*harmine must be represented by XIV



(XIV.)

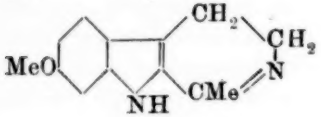


(XV.)

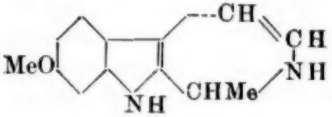
and XV respectively, and since harminic acid is no longer to be regarded as a pyridine-$\alpha\beta$-dicarboxylic acid, the elimination on heating of both carboxyl groups becomes explicable.

The Constitution of Harmaline.

Since harmaline may be oxidised to harmine (Fritzsche, *Annalen*, 1848, **64**, 365; O. Fischer, *Ber.*, 1889, **22**, 640) and reduced to tetrahydroharmine, it is to be regarded as dihydroharmine, and the most probable constitutional formulæ for the base are shown in XVI and XVII. The available evidence does not all point in one direction, but, on the balance, we favour the structure XVI as being the better summary of the relations and properties of the base:



(XVI.)



(XVII.)

In support of the expression XVI the following considerations may be noted *inter alia*.

(1) The harmaline metho-salts, for example, the metho-chloride (see p. 952), are quaternary salts and give no precipitate on the addition of ammonia to their aqueous solutions.

(2) The fact that harmaline occurs in the seeds of *Peganum harmala* in an optically inactive condition is consistent with a formula like XVI, which contains no asymmetric carbon atom, whilst, on the other hand, a base having the constitution XVII, which implies the possibility of the existence of enantiomorphic modifications, would most probably occur in a plant in an optically active condition.

(3) Harmaline shows a tendency to form additive products, for example, with hydroxylamine (O. Fischer, *Ber.*, 1914, **47**, 105) and with hydrogen cyanide (Fritzsche, *Annalen*, 1848, **68**, 351; 1849, **72**, 307). The product of the latter process, cyanodihydroharmaline, is a base, and the whole reaction is reminiscent of that between cotarninium or hydrastinium salts and potassium cyanide. Like cyanohydrocotarnine, cyanodihydroharmaline is resolved into its components on warming with a mineral acid. The ketimino-type structure of XVI furnishes an explanation of these additive reactions.

(4) The oxidation of tetrahydroharmine with production of harmaline (see below) is more readily understood with the aid of the formula XVI than with XVII.

The more important arguments in favour of XVII are the following:

(1) Harmaline forms an acetyl derivative and an *N*-methyl derivative closely resembling the parent base.

(2) Harmaline condenses with diazonium salts with formation of bisazo-compounds (O. Fischer and W. Boesler, *Ber.*, 1912, **45**, 1930). On the assumption that XVII is correct, this behaviour is explicable since one point of coupling would be in the benzene ring as in the case of tetrahydroharmine, whilst the second point of attack is in the group ·CH:CH·NH·, which is contained as such or in a homologous form in many non-benzenoid substances which form azo-derivatives on treatment with diazonium salts.

(3) The possibility of migration of the ethylene linking may be held to discount to some extent the arguments 1 and 2 advanced in support of formula XVI.

A formula for harmaline must be grounded on a knowledge of the constitution of harmine, and until the position of the methyl group in the latter is known with a greater approach to certainty it is impossible to be quite sure that there is no alternative to the suggestions which have been discussed.

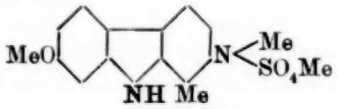
Harmaline forms a normal methosulphate which is readily oxidised by potassium permanganate in acetone solution (see p. 960), yielding the substance (m. p. 228°) mentioned above as the oxidation product of *N*-methyltetrahydroharmine. There is therefore an interdependence between the constitutions assumed for harmaline and for the substance melting at 228°. Formula XVI for harmaline corresponds with XII for the oxidation product, whilst XIII for this substance and XVII for harmaline are similarly related.

Methylharmine.

It has been tacitly assumed that the basic nitrogen of harmine is that which is contained in the pyridine nucleus, and the basis of this theory may now be more particularly stated. Harmine closely resembles carbazole in constitution, and the nitrogen atom of carbazole is almost devoid of basic character, so that the similarly situated nitrogen of the imino-group of harmine should also lack salt-forming character. This point of view is supported by the fact that harmine is similar to carbazole in the degree of reactivity of its benzene nucleus and by the correspondence in properties between tetrahydroharmine and a dialkylindole. Again, the metho-salts of harmine are quaternary salts, so that they can scarcely have been formed by addition to an imino-group, and these salts exhibit the

same fluorescence in aqueous solution as a harmine salt. Finally, *N*-acetyltetrahydroharmine is not a base.

Accordingly, if harmine is VI, harmine methosulphate (p. 951), which is typical of the harmine metho-salts, must be represented by the formula XVIII:



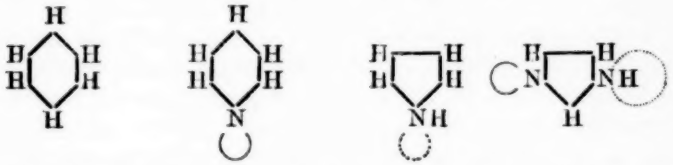
(XVIII.)

An aqueous solution of this salt gives no precipitate with ammonia or even with very dilute sodium hydroxide, but, on the addition of more sodium hydroxide, a yellow, chalky precipitate is obtained, and this appears to have the composition $C_{14}H_{14}ON_2,3H_2O$, and is probably the quaternary ammonium hydroxide corresponding with XVIII with two molecules of water of crystallisation. By heating at 100° this hydrated material is changed into methylharmine melting at 209° (compare O. Fischer, *Ber.*, 1897, **30**, 2482). The salts of this substance with acids are identical with the corresponding metho-salts of harmine, and it is reconverted into the ammonium hydroxide by boiling with water. There are three possible ways of representing the elimination of water from harmine methohydroxide with the formation of methyl harmine. In the first place a group, $:N:CH_2$, might be formed, but this would result in an unusual type of quinquevalent nitrogen, and if this were the true explanation the loss of water from methylpyridinium hydroxides and methylquinolinium hydroxides with the formation of methylpyridines and methylquinolines might be anticipated. The second view might be that the C-methyl group is involved, $\cdot C(CH_3):NMe(OH)\cdot$, being changed into $\cdot C(:CH_2)\cdot NMe\cdot$. This possibility is excluded by the observation (p. 951) that norharmine methosulphate on decomposition with hot aqueous sodium hydroxide yields a methylnorharmine entirely resembling methylharmine. The third and only remaining alternative quite free from objection is that water is eliminated by the combination of the hydroxyl of the quaternary ammonium hydroxide and the hydrogen of the imino-group in the pyrrole nucleus. This leads to the formulæ XIX and XX for methylnorharmine and methylharmine respectively:

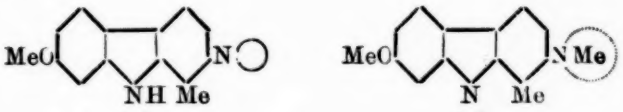
(XIX.)

(XX.)

These formulæ are based on a conception of the nature of aromatic types which is comparable to that expressed in the Kekulé benzene formula, and it is on this account that the arrangement of the valencies appears somewhat unusual and the close relation with harmine is obscured. If, however, the symbols



are employed for benzene, pyridine, pyrrole, and glyoxaline respectively, the corresponding expressions for harmine and methylharmine are XXI and XXII, and it will be seen that the difference between the ring-systems is almost confined to the function of the nitrogen atoms. The thickened lines in all these formulæ represent a sesqui-valency and the dotted loops attached to the nitrogen atoms indicate that a partial use for nuclear conjugation has been made of the latent valencies.



(XXI.) (XXII.)

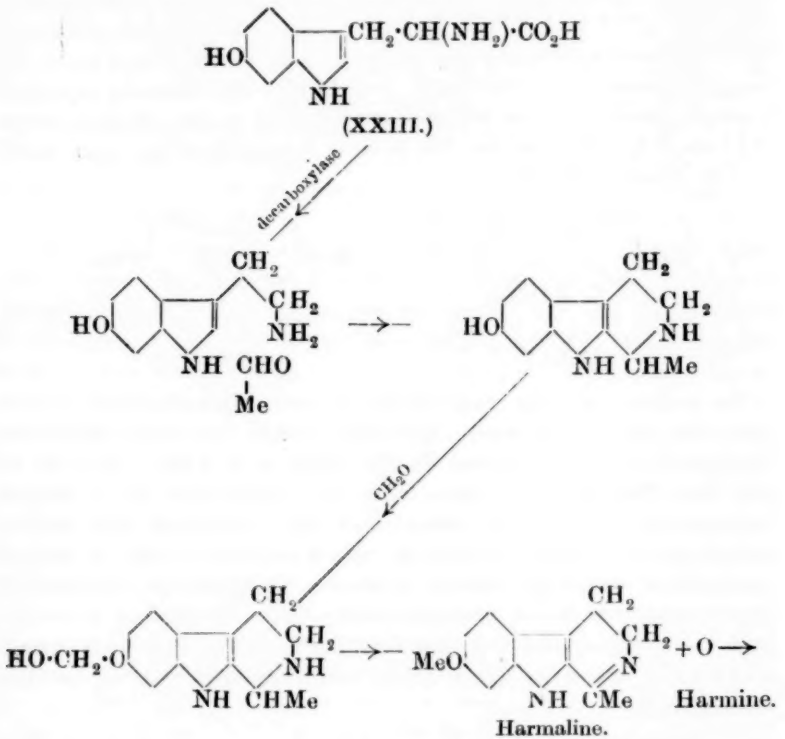
On gently warming with sulphuric acid, methylharmine is sulphonated and an extremely sparingly soluble, colourless substance, $C_{14}H_{14}O_4N_2S$, is precipitated on the addition of water. In view of the fact that methylharmine may be regenerated by prolonged boiling with dilute hydrochloric acid, this compound may be the anhydride of harmine methohydroxide *N*-sulphonic acid. A similar pale yellow, sparingly soluble substance, $C_{14}H_{16}O_4N_2S$, is obtained by warming harmaline methochloride with concentrated sulphuric acid and pouring the solution into water. The sulphonic group may also be in the benzene nucleus, and the matter is being further investigated.

The Synthesis of Harmine and Harmaline in the Plant.

One of the strongest arguments in favour of the main outlines of the views which have been developed above is that, unlike the older formulæ, the new expressions contain a ring-system which is related to that of an important and widely distributed amino-acid, namely, tryptophan. The actual starting point is, however, not

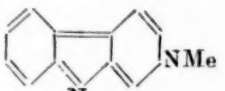
tryptophan itself, but a hydroxytryptophan bearing the relation to the former substance which tyrosine bears to phenylalanine. We venture to predict that this hydroxytryptophan (XXIII) will be found among the amino-acids derived from vegetable proteins.

Abderhalden and Baumann (*Zeitsch. physiol. Chem.*, 1908, **55**, 412) have, indeed, already stated that tryptophan is generally found in combination with a hydroxytryptophan, but it does not appear that a description of this substance has been published, and there is no evidence that the hydroxyl group is in the benzene ring. The elaboration of hydroxytryptophan (XXIII) into harmine is shown in the following scheme, and is strictly parallel with the phytochemical synthesis of an *iso*quinoline alkaloid:

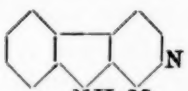


The acetaidehyde required probably arises from the oxidation of alanine. This scheme implies the production of the tetrahydroharmine ring in the first place, and this later becomes oxidised to harmaline and harmine. In this connexion experimental evidence is not lacking since we have found (p. 961) that tetrahydroharmine may be oxidised to harmaline by means of potassium permanganate

in acetone solution and the further oxidation of harmaline to harmine has also been effected (*loc. cit.*). Thus by oxidation of tetrahydroharmine the intermediate stage can be realised, whilst harmaline has never been detected as one of the products of reduction of harmine. Indeed, the conversion of harmine into harmaline by any process has never previously been possible and has only become practicable through the intermediary of tetrahydroharmine, which is obtainable from harmine. The crystalline base, $C_{12}H_{10}N_2$, which Hopkins and Cole (*J. Physiol.*, 1902, **29**, 451) obtained from tryptophan by oxidation with ferric chloride may possibly owe its formation to a reaction similar to that assumed above in the vital synthesis of harmine. It is clear that the carboxyl group of tryptophan has been eliminated, and therefore C_2 has been added, and this may be due to the presence of formaldehyde (2 mols.) or of some oxygenated ethane derivative or the equivalents of these derived from a degradation of a second molecule of tryptophan. The two most probable formulæ are XXIV and XXV, and, since the base melts at 238°, perhaps the latter is preferable, as this melting point would be rather high for an *N*-methyl derivative of this type. Thus harmine melts at 257° and methylharmine at 209°; harmaline melts at 238° and methylharmaline at 162°; *apo*harmine melts at 183° and methyl*apo*harmine at 78°:



(XXIV.)



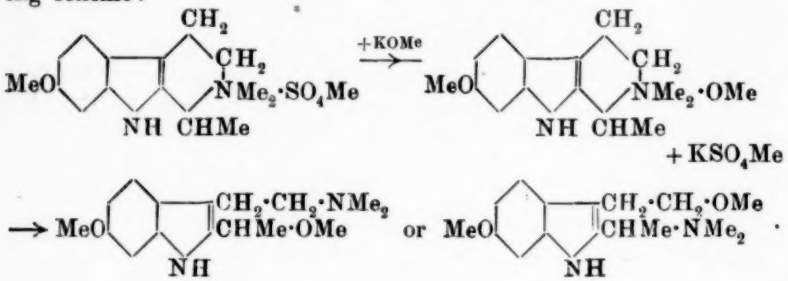
(XXV.)

Formula XXV is, however, the constitution on the basis of our views of harman which melts at 230° (O. Fischer, *Chem. Centr.*, 1901, i, 957), and in spite of this difference in melting point we consider there is a possibility that the two substances may be identical.

A Ring-fission of a Harmine Derivative.

Up to the present the harmine ring has resisted all attempts to open it without loss of carbon or nitrogen, and on this account especial interest attaches to the investigation of a colourless base (m. p. 129°), which O. Fischer first prepared by the decomposition of methyltetrahydroharmine methiodide by means of methyl-alcoholic potassium hydroxide (*Ber.*, 1914, **47**, 104). We have obtained the same substance from the normal methosulphate of methyltetrahydroharmine, by boiling with methyl-alcoholic potassium hydroxide, but find its composition to be $C_{16}H_{24}O_2N_2$, instead of $C_{15}H_{22}O_2N_2$, as suggested by Fischer. A Zeisel estimation

showed the presence of two methoxyl groups, so that the additional carbon atom is most probably derived from the methyl alcohol used as solvent, and this was confirmed by the fact that when ethyl-alcoholic potassium hydroxide was employed in the reaction a new substance, $C_{17}H_{26}O_2N_2$, was obtained. Unfortunately, the latter compound could not be crystallised, but the analytical results were sufficiently satisfactory to establish the point at issue. The base (m. p. 129°) is produced in our view in accordance with the following scheme:



The fact that ethers of this kind are readily formed has been demonstrated by M. Scholtz (*Ber.*, 1913, **46**, 2138), who found that aldehydes react with 2-methylindole in alcoholic solution in the presence of sodium hydroxide with the formation of substances of the type

$$OEt\cdot CHR\cdot C\begin{<}C_6H_4\\CMe\end{>}NH.$$

Experimental.

Harmine Metho-salts.

Harmine Methosulphate, $C_{13}H_{12}ON_2,Me_2SO_4$.—This derivative is readily prepared by rubbing harmine (1 gram) into a paste with methyl sulphate (1 c.c.), leaving for twenty-four hours, and then dissolving the solid product in boiling methyl alcohol. On cooling, the methosulphate separates as a pale yellowish-green, crystalline mass, and, after repeated recrystallisation, is obtained almost colourless. In preparing larger quantities, a good plan is to cover the finely powdered harmine with benzene, and, after adding the methyl sulphate, to heat on the steam-bath, when combination takes place rapidly and is complete in half an hour. The product is washed with benzene by the aid of the pump and drained on porous porcelain. A specimen, which had been crystallised from water and left exposed to the air until dry, yielded the following analytical results:

0·1288 lost 0·112 at 100°. $H_2O=8·7$.

*0·1176 gave 0·2316 CO_2 and 0·0580 H_2O. $C=53·7$; $H=5·3$.

$C_{13}H_{12}ON_2,Me_2SO_4,2H_2O$ contains $H_2O=9·6$ per cent. and $C_{13}H_{12}ON_2,Me_2SO_4$ requires $C=53·3$; $H=5·3$ per cent.

Harmine methosulphate melts at about 220° and is readily soluble in hot water, from which it separates as a voluminous mass of needles; it is also readily soluble in boiling methyl alcohol, but much less so in the cold. The aqueous solution is not precipitated by ammonia, but sodium hydroxide gives at once a voluminous, yellow, crystalline precipitate of the hydrated ammonium hydroxide (see p. 948).

Harmine Methiodide, $C_{13}H_{12}ON_2,MeI$.—This substance, first prepared by O. Fischer and E. Taüber (*Ber.*, 1885, **18**, 402) by the direct addition of methyl iodide to harmine, is conveniently obtained in the following manner. Harmine methosulphate (5 grams) dissolved in boiling water (150 c.c.) is mixed with boiling dilute potassium iodide (5 grams), when an immediate voluminous, almost colourless precipitate separates; this is collected and crystallised from alcohol, from which it separates in needles. When rapidly heated it darkens at 290° and melts at 305—307° to a black mass.

Harmine Methochloride, $C_{13}H_{12}ON_2,MeCl$.—This characteristic derivative is obtained when harmine methiodide, ground into a paste with much hot water, is digested on the steam-bath with a considerable excess of freshly prepared silver chloride. After filtering, the nearly colourless filtrate is concentrated and left overnight, when the liquid becomes filled with a mass of very pale yellow needles which exhibit a slight green fluorescence. The air-dry substance gave the following analytical results:

1·4307, heated at 100°, lost 0·2769. $H_2O=19·4$.

*0·1234 gave 0·2905 CO_2 and 0·0631 H_2O. $C=64·2$; $H=5·7$.

$C_{13}H_{12}ON_2,MeCl,4H_2O$ contains $H_2O=21·5$ and $C_{13}H_{12}ON_2,MeCl$ requires $C=64·0$; $H=5·7$ per cent.

Harmine methochloride, when rapidly heated, scarcely darkens at 280° and melts at about 305° with effervescence to a black froth; it is rather sparingly soluble in boiling methyl alcohol and separates well in colourless groups of slender, prismatic needles. Its aqueous solution fluoresces blue and resembles the methosulphate in its behaviour with ammonia and sodium hydroxide.

Methylharmine (Formula XX or XXII).

This substance, first prepared by O. Fischer (*Ber.*, 1897, **30**, 2482) from harmine methiodide by treatment with potassium hydr-

* Dried at 100°.

oxide, is described as a colourless substance which melts at 209°, crystallises from benzene in needles, and rapidly absorbs carbon dioxide from the air. We have prepared methylharmine from harmine methosulphate and methochloride by the action of sodium hydroxide. The aqueous solution of either of these derivatives gives a voluminous, yellow precipitate on the addition of sodium hydroxide in the cold, and this is readily soluble in hot water and separates, on cooling slowly, in long, very pale yellow needles. After twice crystallising from water, the substance was left for three days exposed to the air and then analysed:

I. 1·1407, heated at 100°, lost 0·1999. $H_2O=17·5$.
0·1033 gave 0·2350 CO_2 and 0·0668 H_2O. $C=62·0$; $H=7·2$.
$C_{14}H_{14}ON_2,3H_2O$ requires $H_2O=19·3$; $C=60·0$; $H=7·1$ per cent.

II. Two specimens, heated at 100° until constant, gave the following analytical results:

0·1172 gave 0·3181 CO_2 and 0·0649 H_2O. $C=74·0$; $H=6·2$.
0·1286 ,, 0·3506 CO_2 ,, 0·0715 H_2O. $C=74·3$; $H=6·3$.
$C_{14}H_{14}ON_2$ requires $C=74·3$; $H=6·2$ per cent.

It is clear that the substance precipitated from harmine methosulphate or methochloride by sodium hydroxide is a hydrate of the probable composition, $C_{14}H_{14}ON_2,3H_2O$, and that this loses all its water at 100°, leaving pure methylharmine which, as stated by Fischer, melts at 209°. The following experiment supports the view that the hydrate crystallised from water is harmine methohydroxide with $2H_2O$. When the hydrate is exposed over sulphuric acid in a vacuum desiccator it rapidly loses $2H_2O$ and the last H_2O with much greater difficulty. Thus a specimen which had been exposed in the desiccator for six hours yielded $C=69·0$; $H=6·7$; after twenty-four hours it contained $C=70·8$; $H=6·4$, and after two days $C=71·5$; $H=6·2$, whereas $C_{14}H_{14}ON_2,H_2O$ requires $C=68·8$; $H=6·4$ per cent.

Exposure to the air did not in our experience lead to the formation of carbonate as suggested by O. Fischer, since, after seven days' exposure, there was no effervescence on the addition of hydrochloric acid. Also analytical results are recorded above for air-dried material, and these were apparently not vitiated by absorption of carbon dioxide. *Methylharmine hydrochloride* is obtained as a sparingly soluble precipitate when the above hydrate is mixed with dilute hydrochloric acid. It crystallises from boiling dilute hydrochloric acid as a voluminous mass of needles, melts and decomposes at 305°, and is identical with harmine methochloride. (Found, $C=64·1$; $H=5·8$. $C_{14}H_{14}ON_2,HCl$ requires $C=64·0$; $H=5·7$ per cent.)

Methylharmine Methosulphate, $C_{14}H_{14}ON_2,Me_2SO_4$.—Methylharmine reacts with methyl sulphate with the evolution of much heat and, in preparing the methosulphate, it is necessary either to employ small quantities of material or to use a diluent, such as benzene. When methylharmine (1 gram) is rubbed with methyl sulphate (1 c.c.), a stiff, chalky paste is soon formed and, after remaining overnight, the product is recrystallised from methyl alcohol, in which the methosulphate is unusually sparingly soluble and from which it separates as a voluminous mass of colourless needles:

0·1107 gave 0·2221 CO_2 and 0·0580 H_2O. C = 54·7; H = 5·8.
$C_{14}H_{14}ON_2,Me_2SO_4$ requires C = 54·6; H = 5·7 per cent.

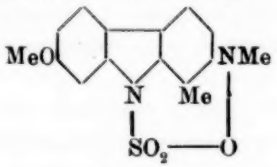
Methylharmine methosulphate is readily soluble in water and both the aqueous and methyl-alcoholic solutions, especially when dilute, exhibit a beautiful, pure blue fluorescence. It separates from a concentrated aqueous solution in felted needles. The solution in acetic acid gives, on the addition of sulphuric acid, a yellow liquid with a striking green fluorescence reminiscent of that of alkaline fluorescein; after a time the yellow colour and the fluorescence disappear, and the addition of a drop of dilute nitric acid produces a reddish-violet coloration. In concentrated sulphuric acid a similar fluorescent solution is obtained, and, on gently warming, this very rapidly fades and a colourless solution with violet fluorescence results. On the addition of water an extremely sparingly soluble precipitate consisting of colourless, satiny needles is formed. This substance contains sulphur, but differs from the sulphonic derivatives described on pp. 950, 953 in not being affected by aqueous sodium hydroxide even on boiling. The aqueous solution of the methosulphate is coloured yellow by potassium hydroxide, and, on heating to boiling, the yellow colour disappears, and if cooled much of the methosulphate separates unchanged. If, however, the boiling is continued for some time, a substance separates on cooling which appears to be the corresponding ammonium hydroxide. This was collected and dissolved in a large excess of boiling dilute hydrochloric acid, from which *methylharmine methochloride*, $C_{14}H_{14}ON_2,MeCl$, separated as a voluminous mass of colourless needles:

0·1108 gave 0·2631 CO_2 and 0·0615 H_2O. C = 64·8; H = 6·2.
$C_{14}H_{14}ON_2,MeCl$ requires C = 65·1; H = 6·7 per cent.

This methochloride becomes yellow at 270° and melts at about 280—285° with effervescence to a reddish-brown syrup. The aqueous solution exhibits a fine blue fluorescence and becomes yellow on the addition of ammonia or sodium hydroxide, but no precipitate sepa-

rates. When, however, the aqueous solution, rendered strongly alkaline by sodium hydroxide, is boiled and concentrated, it deposits a pale yellow, crystalline precipitate, which dissolves in dilute hydrochloric acid with regeneration of the methochloride.

Harmine Methohydroxide Sulphonic Anhydride,



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On one occasion, in preparing harmine methosulphate at 100° in an open vessel, it was noticed that instead of the expected product a very sparingly soluble, colourless substance was formed, and this result was traced to hydrolysis of the methyl sulphate and formation of sulphuric acid, which even under these conditions readily sulphonated the harmine methosulphate. It was then found that the same substance could be obtained by treating methylharmine in acetic anhydride with a few drops of sulphuric acid and by warming harmine methosulphate with concentrated sulphuric acid. A theoretical yield was obtained in the following manner. Harmine (5 grams) was finely powdered and heated during an hour on the steam-bath with toluene (20 c.c.) and methyl sulphate (15 c.c.), concentrated sulphuric acid (10 c.c.) was then added and the heating continued during half an hour. After the addition of water the precipitate was collected and dissolved in dilute sodium hydroxide. The filtered solution was diluted to 2000 c.c., heated to boiling, and acidified by the addition of hydrochloric acid. Almost immediately the substance crystallised from the solution in colourless, microscopic needles, which were collected, washed with hot water, and dried at 100°:

0·1301 gave 0·2629 CO_2 and 0·0545 H_2O. C = 55·1; H = 4·7.

0·1272 „ 0·0958 $BaSO_4$. S = 10·3.

$C_{14}H_{14}O_4N_2S$ requires C = 54·9; H = 4·6; S = 10·5 per cent.

This compound is very sparingly soluble in organic solvents and in water. It dissolves to some extent in boiling dilute hydrochloric acid and separates on cooling in an unchanged condition. Its solution in concentrated sulphuric acid is colourless, and exhibits a bluish-violet fluorescence. It is readily soluble in aqueous sodium hydroxide to a yellow solution, from which acids precipitate the original substance, but it is not attacked by cold sodium carbonate. A small quantity was boiled with dilute hydrochloric acid during

fourteen successive working days, when it was noticed that the amount which had separated, on cooling overnight, became smaller and smaller. On the addition of sodium hydroxide a precipitate was obtained, and this was collected and crystallised from benzene, when pale yellow needles of methylharmine melting at 209° were obtained. It is also possible to hydrolyse the substance with the formation of harmine. It slowly dissolved in boiling glycerol, and on pouring the solution into water only a small amount of insoluble material remained in suspension. The filtered liquid was mixed with sodium hydroxide, the precipitate collected and crystallised from alcohol. The colourless needles so obtained melted at 256° alone or when mixed with a specimen of pure harmine.

Methylnorharmine (Formula XIX).

Norharmine (2 grams) (Perkin and Robinson, T., 1912, **101**, 1786) was dissolved in the minimum quantity of boiling benzene and methyl sulphate (5 c.c.) added to the solution, which was not again heated. The methosulphate soon separated as an oil, which later crystallised, and after leaving overnight the benzene was decanted and the solid washed with ether and then dissolved in water. The colourless solution exhibited blue fluorescence, and on the addition of an excess of sodium hydroxide a yellow, chalky precipitate was obtained. This was collected, dried in a vacuum desiccator over phosphoric oxide, and crystallised from dry benzene. The very pale yellow, flat needles melted at 195—196° with slight previous softening:

0·1049 gave 0·2832 CO_2 and 0·0549 H_2O. C = 73·6; H = 5·8.
$C_{13}H_{12}ON_2$ requires C = 73·6; H = 5·7 per cent.

Methylnorharmine is moderately readily soluble in alcohol, but sparingly so in benzene; it also dissolves in boiling water and crystallises on cooling, probably as norharmine methohydroxide. It has a great superficial resemblance to methylharmine, and dissolves in sulphuric acid to a similar yellow solution with bright green fluorescence. Its solutions in dilute aqueous acids exhibit a blue fluorescence.

Harmaline Metho-salts.

Harmaline Methosulphate, $C_{13}H_{14}ON_2,Me_2SO_4$.—Harmaline combines more energetically with methyl sulphate than does harmine, and the methosulphate is readily prepared by rubbing harmaline (1 gram) with methyl sulphate (1 c.c.), when, even with such small quantities, a considerable rise of temperature will be observed.

After a few hours the yellow mass is crystallised from methyl alcohol, from which the methosulphate separates in yellow needles, and the mother liquor, on the addition of ether, gives a further crop of the same substance. Larger quantities are best prepared, in almost quantitative yield, under the following conditions. Finely powdered and sieved harmaline (30 grams) is covered with benzene (50 c.c.) and mixed with methyl sulphate (30 c.c.), when there is no immediate development of heat, but, on keeping, the temperature gradually rises to about 40°. After remaining for two days, the crystalline mass is collected, washed with benzene, and drained on porous porcelain; it is then pure enough for many purposes:

0·4332 gave 0·2989 $BaSO_4$. S = 9·4.

$C_{13}H_{14}ON_2,Me_2SO_4$ requires S = 9·4 per cent.

Harmaline methosulphate shrinks at 160° and melts at about 170—172° to a deep yellow liquid; it is readily soluble in water or alcohol. The addition of sodium hydroxide to the cold concentrated aqueous solution gives a viscid, orange-red precipitate which, when washed free from alkali and boiled with water, becomes yellow and crystalline, and this substance appears to be nearly pure methylharmaline (compare O. Fischer, *Ber.*, 1897, **30**, 2484; 1914, **47**, 102). The boiling aqueous solution of the methosulphate gives, on the addition of potassium iodide, an immediate yellow, crystalline precipitate of the methiodide, $C_{13}H_{14}ON_2,MeI$. This method of preparation yields at once the pure methiodide, and is therefore to be preferred to the direct combination of harmaline with methyl iodide, since by this latter process dimethylharmaline iodide is also produced (O. Fischer, *Ber.*, 1914, **47**, 104).

Harmaline Methochloride, $C_{13}H_{14}ON_2,MeCl,4H_2O$.—This substance is readily prepared by digesting a paste of harmaline methiodide and much water with an excess of silver chloride on the steam-bath for a couple of hours and filtering. The filtrate is concentrated and allowed to cool slowly, when the methochloride separates as a crust of pale yellow, glistening prisms with a faint green lustre:

*1·0380 lost 0·2223 in the steam-oven. H_2O = 21·6.

†0·1323 gave 0·3097 CO_2 and 0·0786 H_2O. C = 63·9; H = 6·6.

$C_{13}H_{14}ON_2,MeCl,4H_2O$ contains H_2O = 21·4 and $C_{13}H_{14}ON_2,MeCl$ requires C = 63·5; H = 6·4 per cent.

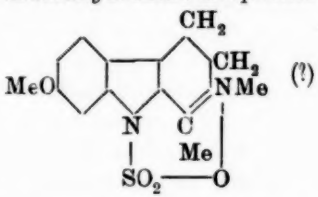
Harmaline methochloride begins to decompose at 260° and melts at about 278° with vigorous effervescence to a reddish-brown froth. It is very readily soluble in hot water or acetic acid, sparingly so in alcohol, and almost insoluble in boiling acetone. The aqueous

* Air-dry. † Dried at 100°.

solution is not precipitated by ammonia, and the bearing of this observation on the constitution of harmaline has been referred to on p. 940. Sodium hydroxide decomposes the salt in aqueous solution and produces an orange-red, viscid mass, which, when washed and boiled with water, becomes yellow and crystalline and doubtless consists of methylharmaline (see above).

The cold aqueous solution of the methochloride instantly decolorises permanganate.

Harmaline Methohydroxide Sulphonic Anhydride,



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When finely divided harmaline methochloride is mixed with concentrated sulphuric acid, it dissolves to an orange-red solution with vigorous evolution of hydrogen chloride. If, after heating on the steam-bath for five minutes, water is added, a substance gradually separates as a voluminous mass of pale lemon-yellow needles. The compound is extremely sparingly soluble in water, but may be crystallised from much boiling water and obtained in long, lemon-yellow needles which become opaque and chalky in the steam-oven. It contains sulphur:

0·1050 gave 0·2108 CO_2 and 0·0494 H_2O. C = 54·7; H = 5·2.

$C_{14}H_{16}O_4N_2S$ requires C = 54·5; H = 5·2 per cent.

This substance is almost insoluble even in boiling acetic acid, it does not melt and scarcely shows any sign of decomposition at 300°. It is not soluble in cold aqueous sodium carbonate, but dissolves on the addition of a drop of sodium hydroxide to a yellow solution, and is precipitated unchanged by hydrochloric acid.

Reduction of Harmaline Methosulphate or the Methochloride: Formation of Methyltetrahydroharmine.

In the first of these reductions, harmaline methosulphate (3 grams), dissolved in dilute sulphuric acid, was reduced in a porcelain beaker fitted with a mechanical stirrer with 3 per cent. sodium amalgam (200 grams), when the colour of the solution gradually faded and the process was completed by heating on the steam-bath. The filtered liquid, rendered alkaline by the addition

of sodium hydroxide, yielded a gummy mass, which soon hardened, and the solution in boiling methyl alcohol deposited, on cooling and stirring vigorously, a mass of glistening plates which, after recrystallisation, melted at 174—176°. This substance has the formula $C_{14}H_{18}ON_2$ (Found, C=72·8; H=8·0; N=12·1. $C_{14}H_{18}ON_2$ requires C=73·1; H=7·8; N=12·2 per cent.), and is evidently identical with the methyldihydroharmaline which O. Fischer (*Ber.*, 1914, **47**, 103) obtained from methylharmaline hydrochloride by reducing in amyl-alcoholic solution with sodium. In the second experiment, which appears to give the purer product, harmaline methochloride (5 grams), dissolved in water (300 c.c.) and hydrochloric acid (50 c.c.), was reduced on the steam-bath by the rapid addition of 3 per cent. sodium amalgam (250 grams). The yellow colour of the methochloride solution rapidly disappeared, and, on adding sodium hydroxide and crystallising the solid base from methyl alcohol, a crust of colourless prisms of methyltetrahydroharmine was obtained which melted directly at 176°.

Methyltetrahydroharmine Methosulphate, $C_{14}H_{18}ON_2,Me_2SO_4$.—When methyltetrahydroharmine (2 grams) is mixed with methyl sulphate (3 c.c.) it dissolves with considerable rise of temperature and the clear syrup suddenly crystallises. A rather better yield is obtained if the base is covered with benzene before mixing with methyl sulphate (see p. 946), when a syrup separates which rapidly crystallises.

The product is then recrystallised from methyl alcohol, in which it is readily soluble and from which it separates as a hard crust of well-developed, colourless prisms *:

0·1049 gave 0·2054 CO_2 and 0·0655 H_2O. C=53·4; H=6·9.
0·1181 ,, 0·2327 CO_2 ,, 0·0688 H_2O. C=53·7; H=6·5.
$C_{16}H_{24}O_5N_2S$ requires C=54·0; H=6·7 per cent.

This methosulphate melts at about 188° without effervescence and is readily soluble in water, yielding a solution which has an extremely bitter taste.

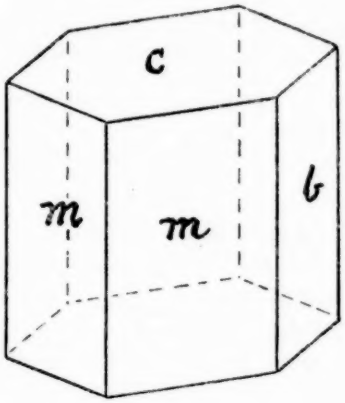
Crystals of methyltetrahydroharmine methosulphate were kindly examined by Miss M. W. Porter, who finds that they are monoclinic with $a:b=0·738$, $\beta=96°55'$. The crystals are of a stout,

* A considerable amount of methosulphate remains in the mother liquors and, if the methyl alcohol is removed by distillation from the steam-bath, most of this decomposes and is converted into a tar.

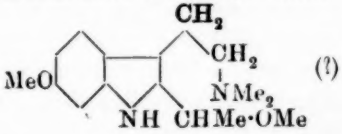
The best plan is to expose the mother liquor over sulphuric acid in a vacuum desiccator, when a hard crust gradually separates mixed with some tar; the latter can be removed by rubbing with cold methyl alcohol and leaving in contact with porous porcelain.

prismatic habit, as shown in Fig. 1, and exhibit the forms $b(010)$, $m(110)$, and $c(001)$. The faces were somewhat curved. Following are the means of the two angles measured: m(azimuth) = 53°47′, c(polar distance) = 6°55′.

FIG. 1.



iso*Methyltetrahydroharmine Methohydroxide Methyl Ether*,



(?)

This substance, which is evidently identical with that obtained by O. Fischer (*Ber.*, 1914, **47**, 104) from the product of the action of methyl iodide on methyltetrahydroharmine by decomposition with methyl-alcoholic potassium hydroxide (compare p. 946), is readily prepared in the following manner: Methyltetrahydroharmine methosulphate (1 gram), dissolved in a little boiling methyl alcohol, is mixed with methyl-alcoholic potassium hydroxide (10 c.c. of 25 per cent.) and boiled for half an hour. Most of the methyl alcohol is then evaporated under reduced pressure and water added, when an oil separates which soon crystallises. The substance is readily purified by recrystallisation from ether, when it separates as a mass of colourless needles or from a mixture of benzene and light petroleum, from which it crystallises in flat needles. In view of the fact that this substance appeared to have a composition different from that ($C_{15}H_{22}O_2N_2$) assigned to it by O. Fischer (*loc. cit.*, compare p. 945), it became necessary to carry out several analyses. The following were made with three different preparations, the first

two having been twice recrystallised from ether and the third from benzene and light petroleum in addition:

I. 0·1067 gave 0·2733 CO_2 and 0·0840 H_2O. C = 69·8; H = 8·7.
0·2093 „ 18·7 c.c. N_2 at 11·5° and 732 mm. N = 10·2.
II. 0·1059 „ 0·2705 CO_2 and 0·0829 H_2O. C = 69·7; H = 8·7.
III. 0·1214 „ 0·3102 CO_2 „ 0·0953 H_2O. C = 69·7; H = 8·7.
$C_{16}H_{24}O_2N_2$ requires C = 69·6; H = 8·7; N = 10·1 per cent.
$C_{15}H_{22}O_2N_2$ „ C = 68·7; H = 8·4; N = 10·7 „ „

The analytical results given by O. Fischer are C = 69·1 and 69·0; H = 8·78 and 8·67; and N = 10·81.

A methoxyl determination by Zeisel's method yielded the following result:

0·2865 gave 0·4790 AgI. MeO = 22·1.
$C_{16}H_{24}O_2N_2$, containing 2MeO, requires MeO = 22·4 per cent.

iso*Methyltetrahydroharmine methohydroxide methyl ether* melts at 128—129° and is readily soluble in alcohol, acetone, or benzene, but sparingly so in water, ether, or light petroleum. It crystallises from dilute methyl alcohol in large, colourless plates or from much light petroleum in groups of flat needles. When it is heated in small quantities it distils with only slight decomposition, but, under 10 mm. pressure, it passes over without residue as a colourless syrup which, when rubbed, solidifies completely. After washing with ether on porous porcelain, the colourless, crystalline mass melted at 121—126° and the admixture with the original substance at 123—126°, showing that no change, such as elimination of water, had taken place during the distillation.

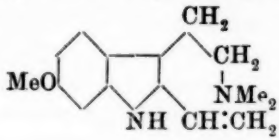
iso*Methyltetrahydroharmine Methohydroxide Ethyl Ether*, $C_{17}H_{26}O_2N_2$.—In order to confirm the composition given for the product of the action of methyl alcohol on methyltetrahydroharmine methosulphate, the latter substance (1 gram) was digested with ethyl-alcoholic potassium hydroxide (10 c.c. of 20 per cent.) for an hour. On adding water, a viscid, ochreous precipitate separated, which was extracted with ether, and the ethereal solution, after thoroughly washing and drying over potassium carbonate, concentrated and left in the ice-chest for a week, but nothing separated.

The ether was then allowed to evaporate slowly over sulphuric acid, when a pasty mass of crystals remained, which was left in contact with porous porcelain until quite dry and hard. As all attempts to recrystallise this substance were unsuccessful, it was dried over phosphoric oxide and analysed:

0·1399 gave 0·3614 CO_2 and 0·1116 H_2O. C = 70·4; H = 8·8.
$C_{17}H_{26}O_2N_2$ requires C = 70·3; H = 9·0 per cent.

When treated with hydrochloric acid and then with potassium iodide, this substance yields a hydrochloride, $C_{15}H_{20}ON_2,HCl$, and hydriodide, $C_{15}H_{20}ON_2,HI$ (m. p. 290—295°), identical with those produced under the same conditions from *iso*methyltetrahydroharmine methohydroxide methyl ether (see below).

Dehydroisomethyltetrahydroharmine Methohydroxide,



, (?) *or its Polymeride.*

The *hydrochloride*, $C_{15}H_{20}ON_2,HCl$, of this base is obtained when *iso*methyltetrahydroharmine methohydroxide methyl ether is treated with dilute hydrochloric acid. The methyl ether dissolves in cold dilute hydrochloric acid, and almost immediately the solution clouds and a caseous substance separates, which soon hardens. This curious salt melts under hot water, dissolves to a pale violet solution, and the addition of hydrochloric acid causes a very pale blue, apparently crystalline, precipitate to separate, which was collected, washed with dilute hydrochloric acid, and dried on porous porcelain over solid potassium hydroxide and then in the steam-oven:

0·1032 gave 0·2415 CO_2 and 0·0707 H_2O. C = 63·8; H = 7·6.
$C_{15}H_{20}ON_2,HCl$ requires C = 64·2; H = 7·5 per cent.

This hydrochloride is readily soluble in water, but sparingly so in dilute hydrochloric acid; the aqueous solution gives on the addition of platinic chloride a pale brown precipitate, which on warming becomes black, and with auric chloride a drab precipitate which becomes violet on heating owing to the separation of metallic gold. When ammonia is added to the solution of the hydrochloride a nearly colourless jelly separates, which is evidently the free dehydro-base (see below).

The *Hydriodide*, $C_{15}H_{20}ON_2,HI$.—The methyl ether dissolves in dilute sulphuric acid at 40°, and, on keeping, the solution clouds and deposits a caseous precipitate of the sulphate, which gradually becomes crystalline.

This was collected, dissolved in warm water, and mixed with potassium iodide, when a sparingly soluble, amorphous precipitate separated, which also became crystalline on warming. After washing well and drying in the steam-oven, this hydriodide was analysed:

0·1089 gave 0·1954 CO_2 and 0·0567 H_2O. C=49·0; H=5·8.
$C_{15}H_{20}ON_2$,HI requires C=48·7; H=5·6 per cent.

On heating in a capillary tube this iodide remains nearly colourless until 250°, then gradually becomes brown, and melts at about 290—295° with vigorous decomposition to a black froth.

Dehydroisomethyltetrahydroharmine methohydroxide was obtained by rubbing the hydriodide to a fine paste with a large excess of dilute ammonia, and, after remaining overnight, the ochreous precipitate was collected and digested at about 60° with a further quantity of dilute ammonia, the process being repeated until no more iodine was removed. The pale ochreous precipitate was collected, thoroughly washed with dilute ammonia, and dried first in a desiccator over phosphoric oxide and then in the steam-oven:

0·1184 gave 0·3182 CO_2 and 0·0874 H_2O. C=73·3; H=8·2.
$C_{15}H_{20}ON_2$ requires C=73·8; H=8·2 per cent.

This curious substance does not melt, and indeed scarcely darkens, at 300°; it dissolves very readily in methyl alcohol, and is precipitated as a pale ochreous precipitate on the addition of ether, but it has not so far been possible to obtain it in a definitely crystalline condition.

Boiling with dilute hydrochloric acid converts it into a sparingly soluble hydrochloride; it dissolves, however, readily in warm glacial acetic acid, yielding a colourless solution which is not precipitated by water. On the addition of ammonia, a colloidal solution is obtained which, on boiling, deposits a flocculent, gelatinous precipitate consisting apparently of the dehydro-base.

The *Methosulphate* and the *Methiodide*, $C_{15}H_{20}ON_2$,MeI.—The solution of *iso*methyltetrahydroharmine methohydroxide methyl ether (1 gram) in benzene (5 c.c.) gives, on the addition of methyl sulphate (1 c.c.), a cloudy liquid: there is considerable development of heat, and a gum separates which is evidently the methosulphate of the dehydro-base. The benzene was decanted, the gum washed with ether, dissolved in hot water and mixed with potassium iodide, when a jelly separated which, on warming, became granular:

0·1147 gave 0·2097 CO_2 and 0·0601 H_2O. C=49·9; H=5·8.
$C_{15}H_{20}ON_2$,MeI requires C=49·8; H=5·9 per cent.

This methiodide does not darken until 260°, and melts at about 290—292° with effervescence to a black froth.

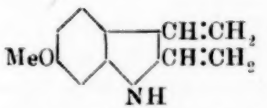
The methosulphate behaves in a remarkable manner when its solution in methyl alcohol is boiled with methyl-alcoholic potassium hydroxide.

Trimethylamine is eliminated but with difficulty, and, on adding water, a milky liquid is produced which gradually deposits a con-

siderable rather viscid precipitate. This was collected and found to be almost insoluble in the usual organic solvents and, after it had been boiled with methyl alcohol, ether, benzene, and finally acetone, a grey mass remained which was exactly similar to india-rubber in appearance and many if its properties.

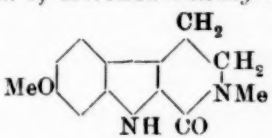
It was resilient like rubber, frothed up on heating to a high temperature, and was quite insoluble in acetic or dilute hydrochloric acid.

There can be little doubt that this mass is a polymeric modification of the divinyl derivative:



but the substance was not further investigated.

Oxidation of Methyltetrahydroharmine and of Harmaline Methosulphate: Formation of Ketoisonormethyltetrahydroharmine,



In studying the oxidation of methyltetrahydroharmine, the base (5 grams), dissolved in acetone (250 c.c.), was gradually treated with very finely powdered permanganate (11 grams) at $-10°$. When the decolorisation of the permanganate, which took place very slowly, was complete the product was filtered, the manganese precipitate thoroughly washed with acetone (*A*), extracted with boiling water, and the dark brown extract concentrated. On neutralising with acetic acid, precipitating with lead acetate, and decomposing the small amount of lead salt with hydrogen sulphide, only 0·5 gram of a dark, resinous acid was obtained, from which nothing crystalline could be isolated. The acetone filtrate (*A*) was concentrated considerably and allowed to remain in the ice-chest, when a heavy, crystalline precipitate rapidly separated, which was collected and washed with methyl alcohol, in which it is almost insoluble.

The substance dissolves in much boiling acetone and separates, on cooling, in glistening, pale lemon-yellow needles:

0·1012 gave 0·2498 CO_2 and 0·0555 H_2O. C = 67·3 H = 6·1.
0·1113 ,, 0·2769 CO_2 ,, 0·0619 H_2O. C = 67·8; H = 6·1.
$C_{13}H_{14}O_2N_2$ requires C = 67·8; H = 6·1 per cent.

Ketoisonormethyltetrahydroharmine melts at 228° and is sparingly soluble in the usual organic solvents. It does not dissolve in dilute mineral acids, and its solution in glacial acetic acid is precipitated by water. Concentrated sulphuric acid dissolves the substance readily to a yellowish-brown solution, but, even after heating on the steam-bath for some minutes, water precipitates much unchanged substance. It is insoluble in cold concentrated hydrochloric acid, but when boiled with the acid it partly dissolves and a crystalline substance separates, which appears to be the hydrochloride and is immediately dissociated on the addition of water. It is also insoluble in aqueous alkalis and in cold methyl-alcoholic potassium hydroxide, but it dissolves in the latter on boiling and crystallises unchanged when the solution is cooled.

Behaviour of Ketoisonormethyltetrahydroharmine with Phosphoryl Chloride and Pentachloride.—That this substance is not readily attacked by these reagents is shown by the following experiment.

When the substance (1 gram) is warmed with phosphoryl chloride (1·5) it is converted into a voluminous, yellow mass consisting probably of the hydrochloride, and if powdered phosphorus pentachloride is now added and the whole heated on the steam-bath a clear liquid is produced.

After heating for fifteen minutes the yellow liquid was poured on powdered ice, when a deep orange, viscid precipitate separated, which was collected, drained on porous porcelain, and rubbed with cold methyl alcohol.

This removes the viscid impurity and leaves a pale ochreous powder, which, after contact with porous porcelain and again washing with methyl alcohol, weighed 0·6 gram, melted at 225—228°, and consisted of unchanged substance.

If the experiment is conducted at a higher temperature than that of the steam-bath some profound change occurs, but the matter has not been further investigated.

Oxidation of Harmaline Methosulphate.—This methosulphate is somewhat sparingly soluble in acetone, even on boiling, and separates in short, well-developed, glistening prisms with bevelled edges. For the purpose of oxidation, the methosulphate (1·5 grams) was dissolved in the least possible quantity of boiling water, mixed with acetone (40 c.c.), and cooled to $-10°$, during which some of the methosulphate separated in a very finely divided condition. Powdered permanganate (2·3 grams) was then gradually added, and so soon as oxidation was complete the whole was filtered and the precipitate, which yields only a trace of acid on extraction with water and acidifying, washed thoroughly with warm acetone. On concen-

trating the acetone extract on the steam-bath, a crystalline mass (0·4 gram) separated which, after recrystallisation from acetone, melted at 227° and consisted of keto*iso*normethyltetrahydroharmine. (Found, C = 67·9; H = 6·1. $C_{13}H_{14}O_2N_2$ requires C = 67·8; H = 6·1 per cent.)

Reduction of Harmaline to Tetrahydroharmine.

Tetrahydroharmine, $C_{13}H_{16}ON_2$ (m. p. 199°), was first prepared by O. Fischer (*Ber.*, 1889, **22**, 637) by the reduction either of harmine or harmaline in alcoholic solution by sodium and later (*Ber.*, 1897, **30**, 2484) in *iso*amyl alcohol solution by sodium. We find that it may be readily prepared by the following simple process: Harmaline (5 grams), dissolved in water (100 c.c.) and hydrochloric acid (20 c.c.), is heated to boiling and then sodium amalgam (300 grams of 3 per cent.) added in three portions, together with further small quantities of hydrochloric acid, so that the liquid is always strongly acid. The deep yellow colour of the harmaline hydrochloride gradually disappears and the solution at the end is almost colourless. On cooling, the sparingly soluble hydrochloride of tetrahydroharmine separates in colourless crusts, and this is collected, dissolved in hot water, precipitated by ammonia, and the base crystallised from methyl alcohol, from which it separates in bundles of needles melting at 198—199°. (Found, C = 72·3; H = 7·6. $C_{13}H_{16}ON_2$ requires C = 72·2; H = 7·4 per cent.) A further quantity may be obtained from the original mother liquors of the hydrochloride, and the total yield is about 90 per cent. of that theoretically possible.

Oxidation of Tetrahydroharmine to Harmaline.—In this experiment tetrahydroharmine (2 grams), dissolved in acetone (150 c.c.), was cooled to −10° and then oxidised by the gradual addition of very finely powdered permanganate (4 grams). The oxidation takes place very gradually, and as soon as the permanganate has been completely decolorised, the whole is filtered and the acetone filtrate concentrated to a small bulk, when a mass of crystals separates which melt at 245° and consist of harmaline, as a mixed melting point and careful comparison of properties clearly demonstrated. (Found, C = 73·2; H = 6·6. $C_{13}H_{14}ON_2$ requires C = 72·9; H = 6·6 per cent.)

Conversion of Tetrahydroharmine into Methyltetrahydroharmine (m. p. 176°).

The methylation of tetrahydroharmine takes place readily under the following conditions: Tetrahydroharmine (3 grams), suspended

in benzene (10 c.c.), is stirred with methyl sulphate (3 c.c.), causing a considerable rise of temperature and separation of a syrup which consists mainly of the methyl hydrogen sulphate of methyltetrahydroharmine.

After twenty-four hours the benzene is decanted, the syrup rubbed and washed with ether, during which it becomes very viscid and stringy, but does not crystallise. This syrup, which contains some tetrahydroharmine methyl hydrogen sulphate or sulphate, was dissolved in water, in which it is very soluble, and mixed with ammonia, when a syrup separated which gradually crystallised. This was collected, dissolved in boiling methyl alcohol, cooled, and vigorously stirred, causing an appreciable amount (about 0·3 gram) of tetrahydroharmine to separate, which was removed by filtration.

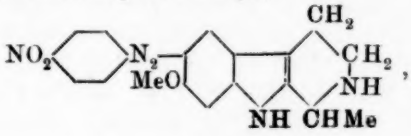
The filtrate was allowed to evaporate and the residual pale brown syrup rubbed with a few drops of methyl alcohol, when it soon began to crystallise and, after remaining in contact with porous porcelain and recrystallisation first from benzene and then from methyl alcohol, a colourless mass of needles was obtained which melted at 174—176°, and consisted of methyltetrahydroharmine (Found: C = 73·3; H = 7·9. $C_{14}H_{18}ON_2$ requires C = 73·1; H = 7·8 per cent.).

The Behaviour of Harmine Derivatives with Diazonium Salts.

Harmine, harmine methosulphate, methylharmine, methylharmine methosulphate, methylharminesulphonic acid, norharmine, and methylnorharmine do not react with benzenediazonium chloride, *p*-nitrobenzenediazonium chloride, or diazobenzenesulphonic acid in aqueous acid, alkaline, or neutral solution. O. Fischer and Boesler (*loc. cit.*) have shown that harmaline forms bisazo-derivatives, and for the sake of comparison with *p*-nitrobenzeneazotetrahydroharmine we prepared the condensation products from harmaline and harmaline methochloride with *p*-nitrobenzenediazonium chloride in dilute acetic acid solution in the presence of sodium acetate. Harmaline gave a dark chocolate-brown precipitate, which appeared slowly and dissolved in concentrated sulphuric acid to a fine, intense royal-blue solution, which, on keeping, became successively dull reddish-purple, reddish-brown, and brown. Harmaline methochloride under similar conditions gave an almost black precipitate, which dissolved in sulphuric acid to a blue solution which, on keeping, became bluish-green, olive-green, and finally dull brown. Methylharmalinesulphonic acid (or harmaline-methohydroxide-sulphonic anhydride) also condenses

with diazonium salts in alkaline solution, and with tetrazotised benzidine yields a dull reddish-purple solution with very deep green fluorescence. On the addition of acid, the solution becomes orange-yellow and the fluorescence disappears, but the alkaline solution dyes cotton in dull mauve shades unaffected by acid. Tetrahydroharmine and *N*-methyltetrahydroharmine condense immediately with diazonium salts in acetic acid solution. With tetrazotised benzidine either of these bases gives a bright red precipitate which dissolves in dilute hydrochloric acid to a reddish-purple, bluish-purple, or pure blue solution according to the concentration of the acid. In concentrated sulphuric acid the solution is pure blue. A dilute acid solution dyes cotton in intermediate shades. The dyed fabric becomes blue if placed in moderately concentrated hydrochloric acid, and on washing with water the colour changes to terra-cotta. Cotton is also dyed terra-cotta by an alcoholic solution of the azo-derivative. With simple benzenediazonium salts, tetrahydroharmine gives yellow to orange precipitates, whilst with those derived from naphthylamines the colour is usually red.

p-*Nitrobenzeneazotetrahydroharmine*,



is obtained as a reddish-brown precipitate on the addition of a solution of *p*-nitrobenzenediazonium acetate to an aqueous acetic acid solution of tetrahydroharmine. Tetrahydroharmine (0·216 gram) was dissolved in water (10 c.c.) and acetic acid (2 c.c.). *p*-Nitroaniline (0·272 gram: 2 mols.) was dissolved in warm concentrated hydrochloric acid (3 c.c.), diluted with water (10 c.c.), and diazotised by the addition of sodium nitrite, after which the solution was made up to 25 c.c. by the addition of saturated aqueous sodium acetate solution. One half exactly of the diazotised *p*-nitroaniline solution was then added to the tetrahydroharmine solution, and after one minute the precipitate was collected, thoroughly washed with water, dried at 100° and in a vacuum over phosphoric oxide until constant. The amount obtained was 0·340 gram, which is a yield of 93 per cent. of the theoretical. The filtrate contained no diazonium salt and, on the addition of the second half of the diazotised *p*-nitroaniline, there was a small precipitation of azo-derivative, but on adding an amount of tetrahydroharmine, dissolved in dilute acetic acid, judged to be approximately 0·2 gram, there was a voluminous precipitate. This experiment proves that the condensation occurs between one molecule of the base and one

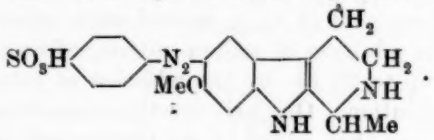
of the diazonium salt. The substance is soluble in boiling alcohol to a crimson solution and, on allowing to cool slowly, the greater part separated in an unsatisfactory condition, but the black powder was mixed with some long, coal-black needles which formed aggregates that could be separated mechanically. These were dried in a vacuum over sulphuric acid and analysed:

0·1147 gave 0·2638 CO_2 and 0·0554 H_2O. C = 62·7; H = 5·4.

$C_{19}H_{19}O_3N_5$ requires C = 62·5; H = 5·2 per cent.

p-*Nitrobenzeneazotetrahydroharmine* melts at 173—175° with decomposition to a black froth. It dissolves in concentrated hydrochloric acid to a crimson solution which becomes orange-red when greatly diluted with water. Unlike the nitrobenzeneazo-derivatives from harmaline and methylharmaline, the solution in sulphuric acid is carmine and does not change appreciably on allowing to remain. The black needles give a chocolate smear on paper, and this exhibits a beetle-green lustre. Methyltetrahydroharmine yields a very similar substance on coupling with diazotised *p*-nitroaniline, whilst methyltetrahydroharmine methosulphate in dilute acetic acid solution in the presence of sodium acetate yields an orange-red solution on the addition of *p*-nitrobenzenediazonium acetate, and this solution becomes blood-red on making alkaline with sodium hydroxide. The base, melting at 129°, obtained from the latter methosulphate by the action of alcoholic potassium hydroxide (p. 956), yields in acetic acid solution an orange-red liquid which becomes carmine on the addition of hydrochloric acid.

Benzeneazotetrahydroharminesulphonic Acid,



Tetrahydroharmine (1 gram) in dilute acetic acid (100 c.c.) was mixed with a solution of diazobenzenesulphonic acid (from 1 gram of sulphanilic acid) when an orange liquid was obtained, and in a few minutes an orange-yellow azo-compound separated in glistening, microscopic prisms. The substance was collected and purified by solution in dilute aqueous sodium hydroxide and precipitation by the addition of acetic acid. The crystals were collected, washed with water, and dried at 100°:

0·2860 gave 0·1658 $BaSO_4$. S = 8·0.

$C_{19}H_{20}O_4N_4S$ requires S = 8·0 per cent.

The substance is not soluble in cold sodium carbonate solution and is very sparingly soluble in organic solvents even in boiling glacial acetic acid. It dissolves in aqueous sodium hydroxide to a bright orange-yellow solution, and this becomes crimson on the addition of hydrochloric acid. The change is very similar to that which is exhibited by methyl-orange when treated in a similar manner, but the harmine derivative gives a more intense coloration. It is, however, not so sensitive an indicator as methyl-orange and requires a higher concentration of hydrogen ion in order to effect the change of colour. A crimson acid solution was diluted with water until the colour had become orange-brown, and on the addition of a trace of methyl-orange the crimson colour was restored. Silk and wool are dyed in pale yellow shades from a suspension of this substance in hot dilute acetic acid.

Benzeneazomethyltetrahydroharminesulphonic Acid.

This substance was prepared from methyltetrahydroharmine in exactly the same way as described above for the corresponding tetrahydroharmine derivatives. The only difference noted was that it crystallised more slowly from solution and had a reddish-brown colour. In acid and alkali it behaved exactly as the substance just described:

0·3142 gave 0·1787 $BaSO_4$. S = 7·7.

$C_{20}H_{22}O_4N_4S$ requires S = 7·8 per cent.

It is an interesting circumstance that the basic nitrogen atom of tetrahydroharmine is not concerned in the coupling with diazonium salts, and this follows from the observation that *N*-acetyl tetrahydroharmine, which does not dissolve in dilute acids, condenses with diazobenzenesulphonic acid in aqueous acetic acid solution with the formation of an azo-derivative which is crimson in acid and yellow in alkaline solutions. The oxidation product of harmaline methosulphate, keto*iso*normethyltetrahydroharmine (m. p. 228°, p. 960), does not condense with diazonium salts.

Colour Reactions for Indole Derivatives applied to Degradation Products of Harmine.

O. Fischer (*Ber.*, 1897, **30**, 2484) noted that tetrahydroharmine colours a pine shaving green in hydrochloric acid solution and that dihydro*apo*harmine (*Ber.*, 1889, **22**, 640) under the same conditions produces an orange colour, but these reactions are not very

characteristic, and we have tried to obtain more definite evidence that harmine is an indole derivative. Almost all the hydro-derivatives give indole indications after fusion with potassium hydroxide, but we specifically mention only those examples which are characteristic. Keto*iso*normethyltetrahydroharmine (m. p. 228°, p. 960), obtained by the oxidation of harmaline methosulphate, is very stable towards fusion with potassium hydroxide, and remains for some time as a yellow or yellowish-brown oil. At a certain point the mixture froths and becomes almost homogeneous and the reaction is then finished. Water is added and the liquid extracted with ether. The colourless, ethereal solution is washed with dilute hydrochloric acid and evaporated, when a small residue is obtained, and this colours a wood shaving blue, in alcoholic hydrochloric acid solution, and gives a deep blue coloration with *p*-dimethylaminobenzaldehyde and aqueous-alcoholic hydrochloric acid on gently warming. The ethereal solution evidently contained a neutral indole derivative, and this was confirmed by treating another portion with concentrated hydrochloric acid and vanillin, when a crimson solution was obtained. Still another portion was dissolved in sulphuric acid to an orange-red solution, which on the addition of a trace of glyoxylic acid (obtained by adding magnesium powder to a concentrated aqueous solution of oxalic acid) became brownish-purple. The hydrochloric acid washings of the ethereal extract were rendered alkaline with sodium hydroxide and extracted with ether. After removal of the solvent the colour reactions just described could be obtained. The fusion of the substance melting at 228°, with potassium hydroxide, results, therefore, in the production of a basic and a neutral indole derivative. The colour obtained with *p*-dimethylaminobenzaldehyde indicates that an α-position has been set free in the indole ring, since scatole gives a blue coloration with this reagent, whilst α-methylindole gives a crimson colour and its methylenedioxy-derivative (Foulds and Robinson, T., 1914, **105**, 1969) almost an identical shade, showing that alkyloxy-groups in the ring are not likely to modify these colour reactions to any great extent. When *iso*methyltetrahydroharmine methohydroxide methyl ether (m. p. 129°, p. 956), obtained from methyltetrahydroharmine methosulphate by the action of methyl-alcoholic potassium hydroxide, is fused with alkali in the presence of air at a high temperature and the product subsequently treated with water, acidified, and the solution evaporated to dryness, a mauve-red coloration is obtained in the test with *p*-dimethylaminobenzaldehyde. This indicates the production of an indole derivative with a free β-position. The base, melting at

129°, and also *N*-acetyltetrahydroharmine yield, beyond question, indole derivatives when warmed with concentrated hydrochloric acid. The acetyl derivative gives a deep greenish-blue coloration when heated with hydrochloric acid and then mixed with an alcoholic solution of *p*-dimethylaminobenzaldehyde.

Either compound when heated with concentrated hydrochloric acid for thirty seconds and then treated with a little vanillin gives a most intense permanganate-coloured solution and, on the addition of water, a purple precipitate. Tetrahydroharmine itself gives a somewhat similar, but far weaker, reaction and a colourless substance separates. On adding water the latter remains unchanged, but most of the colour of the liquid is discharged. With vanillin and hydrochloric acid, α-methylindole gives an orange colour and β-methylindole a blue solution.

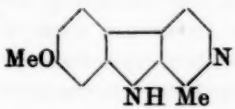
UNIVERSITIES OF OXFORD AND LIVERPOOL.

[*Received, June 23rd,* 1919.]

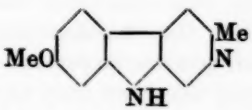
LXXX.—*Harmine and Harmaline. Part IV.*

By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

IN Part III. of this research (this vol., p. 937) it was argued that harmine must be represented by one of the formulæ I or II, and evidence was brought forward which was interpreted in favour of the first of these alternatives:



(I.)



(II.)

The corresponding expressions for the base, harman, which O. Fischer (*Chem. Centr.*, 1901, i, 957) obtained by eliminating the methoxyl group from harmine are III and IV respectively. In the communication already quoted (p. 945) the present authors also considered the question of the probable nature of a base, $C_{12}H_{10}N_2$, prepared by Hopkins and Cole (*J. Physiol.*, 1903, **29**, 451) from

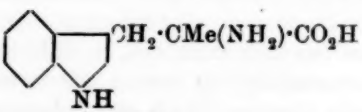
tryptophan by oxidation with ferric chloride, and suggested the representations III and V, of which the former was preferred:

(III.)

(IV.)

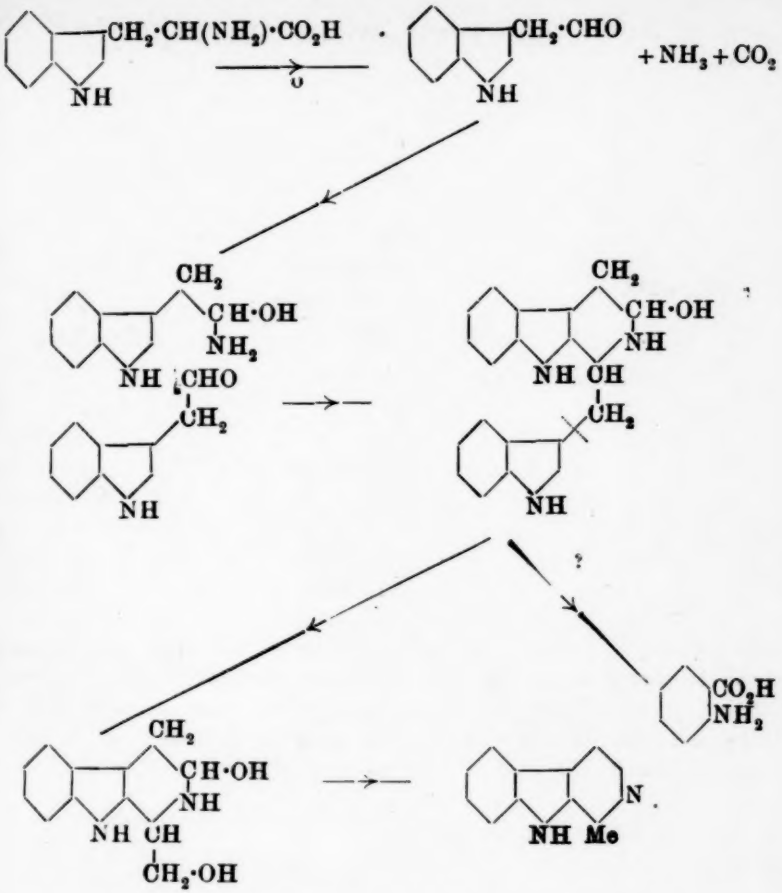
(V.)

The possibility was therefore mooted that the base, $C_{12}H_{10}N_2$ (m. p. 238°), might prove to be harman (m. p. 230° according to O. Fischer, *loc. cit.*), and we are now able to state that this is actually the case. We are greatly indebted to Professor F. Gowland Hopkins, F.R.S., for a specimen of the base, $C_{12}H_{10}N_2$, and, as the result of a careful comparison, we can detect no difference between this substance and harman, the melting point of which we find is also 238°. The details are given in the brief experimental portion appended, and some of the theoretical consequences of this interesting result may now be considered. In the first place this conjunction of the chemistry of harmine and of tryptophan very much strengthens the case for acceptance of the formula I as the best summary of the relations of harmine, since it is almost inconceivable that a substance constituted as IV could arise from tryptophan, even in the presence of other substances. The only loophole is the possible occurrence in some specimens of this amino-acid of a methyltryptophan (VI), which is extremely improbable:



(VI.)

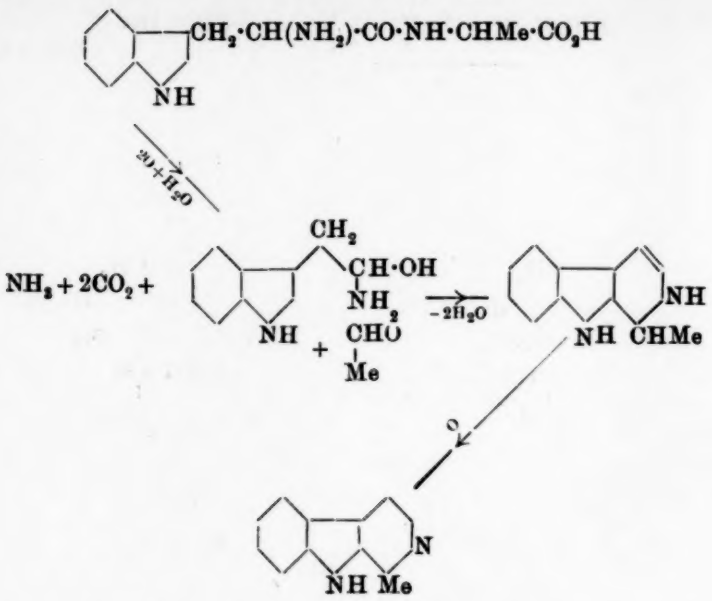
Secondly, the theory put forward in our preceding memoir (*loc. cit.*, p. 944) that harmine originates in nature from a hydroxytryptophan receives important confirmation, since harman may now be so simply obtained from tryptophan in the laboratory. Clearly the mechanism of the latter reaction is a matter worthy of close investigation, since it is probably on analogous lines to the vital synthesis of an alkaloid. One possibility is expressed in the following scheme, in which tryptophan alone is supposed to yield the base and in which the unusual fission, occurring at the point indicated by the dotted line, may find some analogy in the decomposition of tryptophan by *B. coli* resulting in the formation of indole without scatole:



On the other hand, it is more probable that the Me·C group is introduced as the result of the participation in the reaction of some substance which can yield acetaldehyde on oxidation, and as alanine is such a compound it appears feasible to suggest that harman is the result of the oxidation of a mixture of tryptophan and alanine or equivalent dipeptides containing tryptophan and alanine units. The process could then be represented in the manner shown on p. 970.

There are naturally other possibilities, such as the presence of ethyl alcohol or acetic acid.

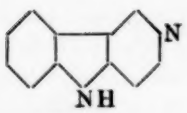
The fused benzene–pyrrole–pyridine nucleus which it now seems certain is contained in the molecule of harmine does not find a place in any approved system of nomenclature, and we therefore suggest



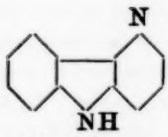
the name '*carboline*'* for this structure, indicating an analogy both to carbazole and quinoline. There are four carboline substitution products and these may be named in accordance with a scheme of numbering which is the same in all cases, and is indicated below in the case of 4-carboline (*nor*harman):

4-Carboline.

3-Carboline.



5-Carboline.



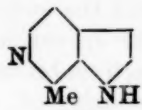
6-Carboline.

Isomeric and probably tautomeric with these are the four '*iso-carbolines*,' the numbering of which need not differ from that of the carbolines. Thus harmine is 11-methoxy-3-methyl-4-carboline,

* The term "carbazoline" has already been used to denote reduction products of carbazole (compare Carrasco, *Gazzetta*, 1908, **38**, ii, 301).

whilst methylharmine (VII, compare this vol., p. 942) is 11-methoxy-3:4-dimethyl-4-*iso*carboline:

(VII.)



(VIII.)

*apo*Harmine, it may be pointed out, has now been shown to be 8-methyl-7-pyrindole (VIII) in accordance with the nomenclature previously suggested (T., 1912, **101**, 1787) for fused pyrrole–pyridine nuclei.

Experimental.

O. Fischer (*loc. cit.*) converted harmine into the corresponding phenol, harmol, by demethylation with concentrated hydrochloric acid in a sealed tube at 140—170°. We have employed this method also, but, in addition, have prepared harmol in almost theoretical yield by boiling harmine with an excess of hydriodic acid (D 1·7) during five hours. On dilution with water and the addition of enough sulphurous acid to remove the free iodine, a crystalline precipitate remained and this was collected and dissolved in dilute aqueous sodium hydroxide. The filtered solution was acidified with acetic acid and the harmol precipitated by the addition of ammonia. The base was at first somewhat viscid, but very soon became granular and crystalline, and was then collected, washed with water, and dried at 100°. Harmol may be converted into harman by careful distillation with a very large excess of zinc dust in a stream of hydrogen, but owing to the high melting point of harmol the yield is unsatisfactory. The crude product from the distillation of 15 grams of harmol, intimately mixed with 250 grams of zinc dust, was dissolved in the minimum of cold concentrated sulphuric acid and the diluted solution mixed with insufficient aqueous ammonia to neutralise the acid. The sparingly soluble sulphate, which separated almost immediately, was collected and decomposed by aqueous sodium hydroxide, when the recovered base, after three crystallisations from benzene, melted at 238°. Harman was also prepared by O. Fischer's method from aminoharman and, as it was thought that the product might be contaminated with ethylharmol, it was boiled with an excess of concentrated hydriodic acid during an hour and the solution diluted, treated with sulphurous acid, and finally with an excess of sodium hydroxide. The precipitated base was collected, crystallised from benzene, and obtained in prisms melting at 238° alone or mixed with a specimen of harman pre-

pared as described above. The specimen of the base $C_{12}H_{10}N_2$ which Professor Hopkins kindly sent us melted at 238° after two crystallisations and the melting point was not depressed by intimate mixture with an approximately equal amount of pure harman. Harman crystallises from benzene in well-defined prisms, the *sulphate*, from dilute sulphuric acid, in radiating clusters of short, delicate, microscopic needles and the *mercurichloride* from dilute hydrochloric acid containing mercuric chloride in long, slender needles. Under the microscope the latter are seen to extend across the field, and each crystal presents the appearance of two sharply defined, straight, parallel lines very close together. The respective crystalline forms and approximate solubilities of the base from tryptophan and its sulphate and mercurichloride were carefully compared with those of harman and the two salts thereof, with the result that complete identity was observed. O. Fischer states that solutions of salts of harman fluoresce blue, but we consider that it is violet, and the shade and intensity of fluorescence were identical in the cases of solutions of harman and of the base from tryptophan. The following experiments were carried out with both specimens and identical results observed. A trace of harman was boiled during five minutes with an excess of methyl iodide, after which the mixture was evaporated to dryness. The pale yellow residue which was sparingly soluble, even in boiling water, was heated with an aqueous suspension of freshly precipitated silver chloride and the solution filtered. The colourless aqueous solution of harman methochloride so obtained exhibited a bluish-violet fluorescence. On the addition of a drop of aqueous sodium hydroxide there was no precipitate, but, on the further addition of sodium hydroxide, a pale yellow precipitate was obtained. On shaking with benzene the latter extracted a bright yellow substance and the solution had a green fluorescence.

The benzene extract was separated and, on the addition of dilute hydrochloric acid, became colourless and the aqueous layer acquired a violet fluorescence. When harman is heated with phthalic anhydride a yellowish-brown fusion is obtained, and, on boiling with alcohol and cooling the solution, a sparingly soluble, orange, crystalline substance separates. The reaction is probably due to a condensation which involves the methyl group in the α-position in the pyridine ring, and harmine exhibits a quite similar behaviour.

UNIVERSITIES OF OXFORD AND LIVERPOOL. [*Received, July 5th*, 1919.]

LXXXI.—*A New Photographic Phenomenon.*

By Donald Neil McArthur and Alfred Walter Stewart.

Although the phenomenon here described has not yet been entirely elucidated, the present preliminary note appears to be justified by the results which have already been obtained. A sensitive photographic plate is placed, film upward, at the bottom of a light-tight box; on the film are placed two or more glass microscope slides, and resting on these supports is laid a negative, also film side upward. The box is then closed and is placed in the neighbourhood of a Bunsen burner, a bat's-wing flame, or an electrical kettle-heater. After an exposure of some hours, the plate after development shows an image of the negative. The resulting photograph is the reverse of the original negative, that is, it is a positive such as would be obtained by simple printing with sensitised paper in the usual way.

In the experiments made, the plates used have been Wellington Anti-screen, Imperial Extra Rapid and Imperial Sovereign makes, different batches of each kind having been employed.

The material of the box may be either wood or cardboard. Care has been taken that no light enters the box; certain of the experiments having been conducted in total darkness, whilst in other cases the openings between the two halves of the boxes have been carefully sealed. The results are obtained whether the box is left in the open air or is enclosed in an air-tight desiccator.

The nature of the source of heat appears to exercise some influence on the rapidity with which the effects are produced. Very poor results are yielded by a Meker burner; poor results are given by a Bunsen flame impregnated with calcium salts; with lithium or sodium salts, the effects are more strongly marked. The electric heater gives very good results when worked on its lower resistance.

The distance between the box and the source of heat has usually been about 30—45 cm., but on one occasion results were obtained with a box placed in a cupboard 180 cm. away from a sodium burner, although in this case the exposure was an extremely prolonged one.

The most striking peculiarity of these experiments is the fact that when the box is arranged so that the sensitive plate lies between the source of heat and the negative, the results are obtained just as sharply as if the negative had been interposed between the heater and the sensitive plate. Were direct-acting rays concerned in the matter, it seems clear that in these circum-

stances the plate would be fogged by their passage through it before they reached the negative at all.

The results are not due to any radioactive material in the neighbourhood, for one of us carried out test experiments in the laboratory of the Queen's University of Belfast, where no radioactive contamination exists, and the effects were obtained there also.

The effects cannot be ascribed to the negative having stored up light which it liberates again in the dark, for a parallel experiment made with a negative which had been specially illuminated for ten minutes within 15 cm. of a spectroscopic spark apparatus gave no results when no source of heat was present.

The rays which produce the effects on the sensitive plate appear to be similar in properties to light rays. Glass is practically transparent to them; inkstains, seccotine, and metal show different degrees of opacity. It has been found that the rays can be diffracted and refracted just like ordinary light.

The matter is being further investigated, but the foregoing is sufficient to show that an interesting field has been opened up.

THE PHYSICAL CHEMISTRY LABORATORY,
GLASGOW UNIVERSITY. [*Received, June 2nd*, 1919.]

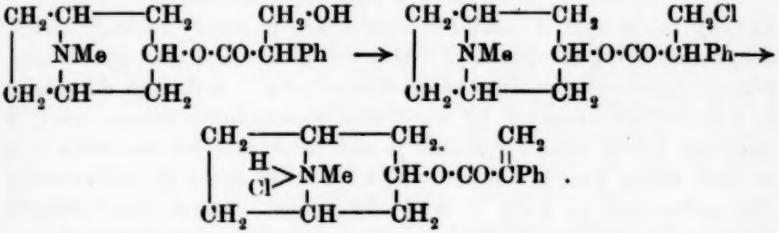
LXXXII.—*The Stereochemistry of Hyoscine.*

By HAROLD KING.

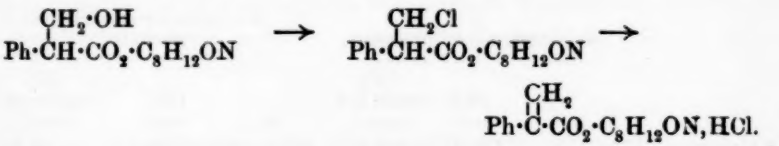
IN a former communication (this vol., p. 476), it was shown that by resolution of a weakly active hyoscine by means of *d*-α-bromo-π-camphorsulphonic acid, *d*-hyoscine bromocamphorsulphonate was obtained as the more sparingly soluble salt. The base proved to be the enantiomorph of the therapeutically valuable *l*-hyoscine of commerce. The unexpected discovery was made, however, that *d*- and *l*-hyoscines gave *dl*-oscine on hydrolysis with acid or alkali, whereas benzoyl-*d*-oscine under similar conditions gave optically pure *d*-oscine. Furthermore, the *d*- and *l*-oscine bases prepared by resolution of *dl*-oscine were not racemised by acid or alkali. On these grounds, *d*- and *l*-hyoscines were regarded as partially racemic esters, the optical activity being solely conditioned by the activity of the tropyl radicle.

In the present communication, further confirmatory evidence is adduced. In 1908, Wolffenstein and Mamlock (*Ber.*, **41**, 730) showed that atropine (tropyltropine) can be converted into

β-chlorohydratropyltropine, and that, on evaporation of the ethereal solution of this base, an intramolecular change takes place, hydrogen chloride being transferred from carbon to nitrogen, with the formation of *apo*atropine hydrochloride.



Willstätter and Hug (*Zeitsch. physiol. Chem.*, 1912, **79**, 146) showed that, in a precisely similar manner, *l*-hyoscine on treatment with thionyl chloride gave β-chlorohydratropyloscine hydrochloride, and the ethereal solution of the base, on evaporation, gave *apo*hyoscine (*apo*scopolamine) hydrochloride.



This reaction destroys the asymmetry of the tropyl group, and could it be carried out under mild conditions, so as to preclude hydrolysis and racemisation, it should indicate whether the oscine portion of the molecule is active or inactive in *l*-hyoscine. Willstätter and Hug, apparently unaware of the significance of this reaction, did not record the polarimetric examination of *apo*hyoscine. Moreover, they used potassium carbonate for liberating the bases from their salts, this alkali being known to racemise *l*-hyoscine partly if contact is at all prolonged (Schmidt, *Arch. Pharm.*, 1898, **47**, 236), and their yield of *apo*hyoscine was only 50 per cent., the loss being attributed to hydrolysis. It has now been found that, on replacing potassium carbonate by the much weaker alkali sodium hydrogen carbonate, the reaction proceeds quantitatively throughout, and the resulting *apo*hyoscine is optically inactive.

To complete the proof of the partial racemic ester nature of *l*-hyoscine, the resolution of *apo*hyoscine has been attempted.

apo*Hyoscine camphorsulphonate* (m. p. 157—158°) is a very readily soluble salt which can be recrystallised from a mixture of alcohol and ether, but shows no signs of resolution. The bromocamphorsulphonate was not obtained crystalline, but the

d-*hydrogen tartrate* crystallises well from water. It contains two molecules of water of crystallisation, melts at 95—97°, and has $[\alpha]_D$ +8·6° in water. Repeated crystallisation failed to change its melting point or its specific rotation.

The results so far obtained are best explained on the assumption already made that *d*- and *l*-hyoscines are partially racemic esters, *d*-hyoscine being composed of *d*-tropyl-*d*-oscine and *d*-tropyl-*l*-oscine, whilst *l*-hyoscine contains the enantiomorphs. Although *d*-hyoscine is not further resolved by *d*-α-bromo-π-camphorsulphonic acid, it does not follow that *l*-hyoscine is not resolvable by the same acid or that either base is not resolvable by other optically active acids. The behaviour of pure *d*- and *l*-hyoscines towards the optically active acids, *d*-camphor-β-sulphonic, *d*-α-bromo-π-camphorsulphonic, and *d*-tartaric has now been investigated, but in no case was there any indication of resolution. The *d*-hydrogen tartrate of *d*-hyoscine could only be obtained as an uncrystallisable syrup.

The properties of the various crystalline camphorsulphonates are shown in the following table:

	d-Camphor-β-sulphonate.			*d*-α-Bromo-π-camphorsulphonate		
	M. p.	$[M]_D$ salt.	$[M]_D$ basic ion (calc.).	M. p.	$[M]_D$ salt.	$[M]_D$ basic ion (calc.).
d-Hyoscine	175—177°	+156·7°	+106·3°	158—160°	+370·5°	+91·8°
l-Hyoscine	186—187°	−40·8°	−91·2°	169—170°	+172·4°	−106·3°

The value obtained by direct observation on *d*- or *l*-hyoscine hydrobromides was $[\alpha]_D \pm 33°$ or $[M]_D \pm 100°$ (this vol., pp. 503, 504).

A peculiar numerical relationship is observable in the calculated molecular rotatory powers of the basic ions, the significance of which is not clear. It suggests a further resolution of *d*- and *l*-hyoscines, but, apart from these values, there is no evidence to support it, the picrate, for instance, prepared from *d*-hyoscine camphorsulphonate, being identical with that prepared from *d*-hyoscine bromocamphorsulphonate.

In addition to the above salts, *l*-hyoscine was found on one occasion to form a labile salt with *d*-α-bromo-π-camphorsulphonic acid. This salt melted at about 150° and had $[\alpha]_D$ +25·5°, $[M]_D$ +157°, but it was not obtained quite pure, as after two crystallisations it became transformed into the ordinary form of higher melting point (169—170°), and subsequent attempts to reproduce it were unsuccessful. Whether the tautomerism is centred in the bromocamphorsulphonic acid portion of the molecule, as has only rarely been observed (Kipping and Tattersall, T., 1903, **83**, 918), or in the hyoscine portion of the molecule, must

for the present remain undecided. In this connexion, however, it is possibly significant that Wentzel (*Dissertation*, cited by Hesse, *J. pr. Chem.*, 1901, [ii], **64**, 274), by crystallising *l*-hyoscine hydrobromide from alcohol, obtained a lævo-hyoscine hydrobromide of much higher rotatory power, namely, $[\alpha]_D$ −32·9°, which fell, on keeping, to −25·8°, the usually observed value. Hesse (*ibid.*, 353) claims to have partly substantiated this observation. This enhanced value for the anhydrous *l*-hyoscine hydrobromide gives a calculated value $[\alpha]_D$ +24·8° for the *d*-α-bromo-π-camphorsulphonate, a value of the same order as that observed, $[\alpha]_D$ +25·5°, for the labile bromocamphorsulphonate described above.

The present author has obtained another *l*-hyoscine bromocamphorsulphonate, $[\alpha]_D$ +17·9°, m. p. 200°, during the resolution of a weakly active hyoscine by means of α-bromo-π-camphorsulphonic acid. The amount of material was, however, only sufficient to prove the identity of the *l*-hyoscine. It is not improbable that the acid contained in this salt is an isomeric acid which was present as an impurity in the original ammonium α-bromo-π-camphorsulphonate used.

Experimental.

Preparation of dl-apo*Hyoscine from* l-*Hyoscine*.

The method employed for preparing this base is a modification of that given by Willstätter and Hug (*loc. cit.*).

l-Hyoscine hydrobromide (3·87 grams) was converted into the base by the use of sodium hydrogen carbonate and chloroform. The chloroform-free base was warmed gently with 10 c.c. of thionyl chloride. The reaction proceeded smoothly, and, after keeping the product overnight, the thionyl chloride was distilled off under diminished pressure, and the last traces were removed by repeated extraction and evaporation with ether. The β-chlorohydratropyloscine hydrochloride was dissolved in a little water, the solution rendered alkaline with sodium hydrogen carbonate, and the base thoroughly extracted with ether. Unlike *l*-hyoscine, this chloro-substituted base could be readily extracted. The ethereal solution was evaporated to dryness, leaving a pale yellow oil, which immediately became opalescent, and, on digesting on the water-bath with fresh ether, no longer dissolved, but commenced to crystallise at the edges. On keeping for two days, it had crystallised completely in rosettes of stout needles consisting of *apo*hyoscine hydrochloride.

A 2·5 per cent. aqueous solution was neutral to litmus, and when examined in a 2-dcm. tube proved to have no action on the plane of polarised light.

The salt (2·7 grams) was dissolved in water (15 c.c.), the solution rendered alkaline with sodium hydrogen carbonate, and the base completely extracted with ether. On removal of the solvent, the base crystallised readily in rhomboidal plates. It melted at 75—78°, and amounted to 2·4 grams. Theory requires 2·5 grams. It was recrystallised from light petroleum (b. p. 40—60°), and separated in magnificent rhomboidal plates. The yield was 2·2 grams, and the base now melted at 79—80° (79—80° corr.).

The base was examined in 2·5 per cent. solution in absolute alcohol in a 2-dcm. tube, but was quite inactive.

Willstätter and Hug record the melting point 97° for *apo*hyoscine base, but this appears to be a misprint for 79°, as the nitrate, picrate, and aurichloride were found to melt at 157° (decomp.), 217—218°, and 188° respectively, in substantial agreement with Willstätter and Hug's recorded values, 157°, 217°, and 183—184° respectively. The appearance and solubilities of the base and these salts were also in agreement. (Aurichloride.—Found: Au = 31·5. $C_{17}H_{19}O_3N,AuCl_3,HCl$ requires Au = 31·5 per cent.).

dl-apo*Hyoscine Camphor-β-sulphonate.*

*apo*Hyoscine base was converted into its salt with camphor-β-sulphonic acid. It crystallised from a mixture of absolute alcohol and ether in irregular-shaped leaflets. It was recrystallised twice, yielding, finally, 0·65 gram melting at 157—158° (160·5—161·5° corr.).

The specific rotation was determined in water.

$c = 2·069$; $l = 2$-dcm.; $\alpha + 0·404°$; $[\alpha]_D + 9·76°$; $[M]_D + 50·5°$.

The value of $[M]_D$ is in excellent agreement with that recorded by Graham (T., 1912, **101**, 747), namely, $[M]_D + 50·4°$ for the camphorsulphonic acid ion. That there was no resolution was confirmed by extracting the base from the solution, which had been used for determining the rotatory power, after rendering alkaline with sodium hydrogen carbonate and examining the solution of the base in absolute alcohol. It had no effect on the plane of polarised light.

The salt with *d*-α-bromo-π-camphorsulphonic acid was not obtained crystalline.

dl-apo*Hyoscine* d-*Hydrogen Tartrate.*

One gram of *apo*hyoscine nitrate was regenerated to base, using sodium hydrogen carbonate and ether. The *d*-hydrogen tartrate

of the base was prepared in aqueous solution by combination with one equivalent proportion (0·45 gram) of *d*-tartaric acid. On concentrating the solution to about 10 c.c., *apo*hyoscine *d*-hydrogen tartrate crystallised in clusters of radiating, white needles. The product was collected and washed with water. When dried in the air, it amounted to 1·15 grams. It was recrystallised four times from water, the properties of the successive fractions being as follows:

I.	1·15 grams,	m. p. 97°,	$[\alpha]_D + 8·74°$.
II.	1·0 gram,	,, 95—97°,	$[\alpha]_D + 8·35°$.
III.	0·75 ,,	,, 95—97°,	$[\alpha]_D + 7·78°$.
IV.	0·45 ,,	,, 95—97°,	$[\alpha]_D + 8·59°$.

Employing Landolt's value, $[M]_D + 42·84°$, for ammonium hydrogen tartrate, the calculated value for *dl-apo*hyoscine *d*-hydrogen tartrate is $[\alpha]_D + 9·1°$, in approximate agreement with the values recorded above. The base when recovered from the fourth fraction was examined in absolute alcohol, but the solution was devoid of optical activity.

dl-apo*Hyoscine* d-*hydrogen tartrate* is sparingly soluble in cold, but dissolves freely in hot water. It crystallises with two molecular proportions of water in clusters of long needles. In a capillary tube it melts at 95—97° (95—97° corr.), and effervesces at 115°, but it melts below 90° when exposed on a watch-glass to a temperature of 90—95°. The water of crystallisation is not lost when the salt is dried in a vacuum over sulphuric acid:

0·1037, air-dried, gave 0·2031 CO_2 and 0·0579 H_2O. C = 53·4; H = 6·2.

$C_{17}H_{19}O_3N, C_4H_6O_6, 2H_2O$ requires C = 53·5; H = 6·2 per cent.

The specific rotation was determined in dilute aqueous solution, using the air-dried salt.

$c = 2·008$; $l = 2$-dcm.; $\alpha + 0·345°$; $[\alpha]_D + 8·6°$; $[M]_D + 40·5°$.

d-*Hyoscine Camphor-β-sulphonate.*

Almost pure *d*-hyoscine base (1·5 grams) was neutralised with camphor-β-sulphonic acid (1·15 grams). The syrupy salt was obtained crystalline by boiling with anhydrous ethyl acetate. It amounted to 2·3 grams and had $[\alpha]_D + 27·6°$. It was recrystallised thrice more from anhydrous ethyl acetate, the specific rotation of the three fractions being successively $[\alpha]_D + 29·5°$, $+ 29·4°$, $+ 29·3°$. The final fraction amounted to 1·5 grams.

d-*Hyoscine camphor-β-sulphonate* crystallises well from anhydrous

ethyl acetate, in which it is sparingly soluble, in elongated, hexagonal-shaped leaflets or in acicular needles. Each fraction examined appeared to contain one molecule of water, which was lost at 95°. The anhydrous salt melted at 175—177° (179—181° corr.).

For the first crops of successive crystallisations, the percentage losses at 95° were 2·95, 3·33, 1·9, 2·95.

$C_{17}H_{21}O_4N,C_{10}H_{16}O_4S,H_2O$ requires $H_2O=3·25$ per cent.

0·1055, dried at 95°, gave 0·2339 CO_2 and 0·0663 H_2O. C = 60·5; H = 7·0.

$C_{17}H_{21}O_4N,C_{10}H_{16}O_4S$ requires C = 60·5; H = 7·0 per cent.

The specific rotatory power of the anhydrous salt was determined in water.

$c=1·994$; $l=2$-dcm.; α +1°10′; $[\alpha]_D$ +29·25°; $[M]_D$ +156·7°.

Employing the value $[M]_D$ +50·4° for the camphor-β-sulphonic acid ion, the calculated molecular rotation of the *d*-hyoscinium ion is $[M]_D$ +106·3°, whence $[\alpha]_D$ +34·9°. The value found by direct observation of *d*-hyoscine hydrobromide was $[\alpha]_D$ +33·2° (this vol., p. 503).

The picrate prepared from the four times recrystallised camphor-β-sulphonate by double decomposition was identical with *d*-hyoscine picrate obtained from *d*-hyoscine α-bromo-π-camphorsulphonate.

d-Hyoscine *d*-hydrogen tartrate was prepared, but all attempts to crystallise it failed.

l-*Hyoscine Camphor-β-sulphonate.*

Pure *l*-hyoscine base (1·4 grams) was neutralised in aqueous solution with Reychler's camphorsulphonic acid (1·0 gram). The dehydrated, syrupy salt was dissolved in anhydrous ethyl acetate, and, on keeping, crystallised homogeneously in clusters of large plates. The salt, when collected, amounted to 1·7 grams, melted at 187—188°, and had $[\alpha]_D$ −7·2°. It was recrystallised twice more, the melting point remaining the same and the rotation being virtually unaltered with $[\alpha]_D$ −8·1° and $[\alpha]_D$ −7·6° successively.

l-*Hyoscine camphor-β-sulphonate* crystallises from anhydrous ethyl acetate in transparent, rectangular plates. It melts at 186—187° (190—191° corr.):

0·2181, dried at 95°, lost nil.

0·0951 gave 0·2117 CO_2 and 0·0588 H_2O. C = 60·7; H = 6·9.

$C_{17}H_{21}O_4N,C_{10}H_{16}O_4S$ requires C = 60·5; H = 7·0 per cent.

The specific rotation was determined in water.

$c=2·006$; $l=2$-dcm.; α −18·33′; $[\alpha]_D$ −7·6°; $[M]_D$ −40·8°.

whence is calculated $[M]_D$ for *l*-hyoscinium ion $-91{\cdot}2°$ and $[\alpha]_D$ $-30{\cdot}0°$.

l-Hyoscine d-α-Bromo-π-camphorsulphonate.

This salt crystallises from anhydrous ethyl acetate in minute needles. The rotation is unchanged after repeated crystallisation, 5·3 grams having $[\alpha]_D$ $+28{\cdot}28°$ yielding, finally, 1·8 grams having $[\alpha]_D$ $+28{\cdot}05°$. It melts, when dried at 110°, at 169—170° (172·5—173·5° corr.). It is deliquescent in a damp atmosphere, and then crystallises in microscopic, rectangular leaflets, probably a hydrated form. The anhydrous salt was analysed, with the following result:

0·2168, dried at 95°, lost 0·0003. Loss = 0·1 per cent.

0·0997, „ 95°, gave 0·1934 CO_2 and 0·0538 H_2O. C = 52·9; H = 6·0.

$C_{17}H_{21}O_4N,C_{10}H_{15}O_4BrS$ requires C = 52·7; H = 5·9 per cent.

The specific rotation was determined in water.

$c = 2{\cdot}026$; $l = 2$-dcm.; α $+1°8{\cdot}2'$; $[\alpha]_D$ $+28{\cdot}05°$; $[M]_D$ $+172{\cdot}4°$.

This gives a value $[M]_D$ $-106{\cdot}3°$ for the molecular rotation of the *l*-hyoscinium ion and $[\alpha]_D$ $-34{\cdot}9°$.

Labile Salt.—On one occasion, a labile form of *l*-hyoscine bromocamphorsulphonate was isolated, the exact conditions being as follows. 7·5 Grams of freshly prepared, syrupy *l*-hyoscine bromocamphorsulphonate were repeatedly evaporated to dryness under diminished pressure with absolute alcohol in order to remove all adhering water. The residue, freed as completely as possible from absolute alcohol, was then dissolved in anhydrous ethyl acetate, and, on keeping for two days, a mixture of two salts separated in what appeared to be approximately equal proportions. One salt had the characteristic crystalline appearance of *l*-hyoscine *d*-α-bromo-π-camphorsulphonate described above, but the other formed tufts of much larger needles with a more glistening appearance. A trace of each was removed, when the former melted at 169—170°, and was thus ordinary *l*-hyoscine bromocamphorsulphonate, whilst the second melted, either air-dried or dried at 100°, at 150°. The whole of the deposit was collected and recrystallised from ethyl acetate. It separated overnight in tufts of silky needles, which melted at 150°, but was contaminated by a much smaller proportion, this time, of ordinary *l*-hyoscine bromocamphorsulphonate, easily discernible as smaller, white tufts of needles. The product amounted to 3·6 grams.

$c = 2{\cdot}068$; $l = 2$-dcm.; α $+1°3{\cdot}4'$; $[\alpha]_D$ $+25{\cdot}5°$.

This value is distinctly less than $[\alpha]_D + 28{\cdot}0°$ observed for ordinary *l*-hyoscine bromocamphorsulphonate. The product was again recrystallised, but gave the ordinary form of *l*-hyoscine bromocamphorsulphonate melting at 169—170°. All attempts again to isolate this labile salt from this particular batch of material were unsuccessful.

l-*Hyoscine Bromocamphorsulphonate*, m. p. 200°.

By resolution of a weakly active hyoscine by *d*-α-bromo-π-camphorsulphonic acid (this vol., p. 502), it was shown that the more sparingly soluble salt was *d*-hyoscine α-bromo-π-camphorsulphonate, and that from the mother liquors a deliquescent salt having a specific rotation approximating to that of a *l*-hyoscine *d*-α-bromo-π-camphorsulphonate could be isolated.

The final mother liquor, on prolonged keeping at a low temperature, deposited 1·65 grams (1·6 per cent. yield) of a salt crystallising in rosettes of rectangular leaflets. It was not deliquescent and melted at 199—200° (203—204° corr.).

The specific rotation was determined on material dried at 95°.

$c = 1{\cdot}943$; $l = 2$-dcm.; $\alpha + 41{\cdot}7'$; $[\alpha]_D + 17{\cdot}9°$.

0·1028 gram, dried at 95°, gave 0·1994 CO_2 and 0·0553 H_2O.

C = 52·9; H = 6·0.

$C_{17}H_{21}O_4N,C_{10}H_{15}O_4BrS$ requires C = 52·7; H = 5·9 per cent.

0·1 Gram of this salt was converted into the picrate, which amounted to 0·09 gram and melted at 183—186°. On recrystallisation, it gave 0·08 gram melting at 185—186°, and when mixed with *l*-hyoscine picrate, no depression in the melting point was observed.

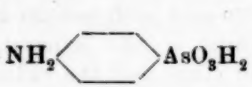
WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.
[*Received, June 27th*, 1919.]

LXXXIII.—*Substituted Phenylarsinic Acids and their Reduction Products, and the Estimation of Arsenic in such Compounds.*

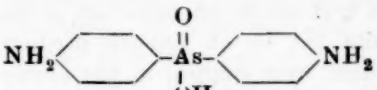
By ROBERT GEORGE FARGHER.

IN the preparation of *p*-aminophenylarsinic acid (I) by Béchamp's method (*Compt. rend.*, 1863, **56**, 1173), Pyman and Reynolds (T., 1908, **98**, 1180) isolated as a by-product a small proportion of

bis-*p*-aminophenylarsinic acid (*pp'*-diaminodiphenylarsinic acid) (II).

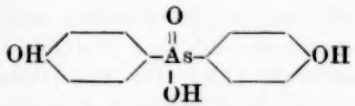


(I.)

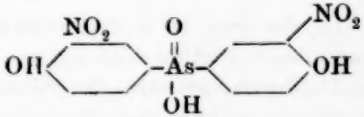


(II.)

In view of the close relation existing between the two acids and the importance of the former as the starting point for the preparation of salvarsan, it seemed to be of interest to prepare the corresponding 3 : 3'-*dinitro*-4 : 4'-*dihydroxydiphenylarsinic acid* (IV) and to examine its reduction products.

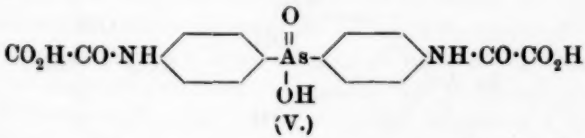


(III.)

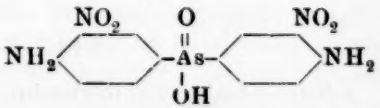


(IV.)

For the preparation of this acid, the two methods described for 3-nitro-4-hydroxyphenylarsinic acid (Bertheim, *Ber.*, 1911, **44**, 3092; Benda and Bertheim, *loc. cit.*, 3445; Benda, *loc. cit.*, 3449) can be used. In the first, the amino-acid (II) is converted into the corresponding hydroxy-acid (III) (Benda, *Ber.*, 1908, **41**, 2371) and subsequently nitrated under suitable conditions. This method gives excellent results. In the second, the amino-acid is converted into its *oxalyl* derivative (V), which is nitrated, the oxalyl group removed by acid hydrolysis, and the amino-group in the resulting 3 : 3'-*dinitro*-4 : 4'-*diaminodiphenylarsinic acid* (VI) subsequently replaced by hydroxyl by alkaline hydrolysis. The usefulness of this method is marred, however, by the fact that at temperatures approaching 140°, oxalic acid causes fission of the molecule of *pp'*-diaminodiphenylarsinic acid to some extent, the product being a mixture from which the pp'-*dioxalylaminodiphenylarsinic acid* can be isolated by means of the sparing solubility of its barium salt in cold dilute ammoniacal solution.

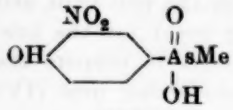


(V.)

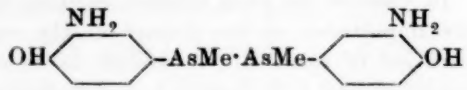


(VI.)

Bertheim (*Ber.*, 1915, **48**, 352), who described the preparation and reduction of 3-nitro-4-hydroxyphenylmethylarsinic acid (VII), found that the direct reduction of the nitro-acid with sodium hyposulphite led to an impure product, whilst if the hyposulphite reduction were stopped at the amino-acid stage and the reduction continued with hypophosphorous acid, 3:3′-diamino-4:4′-dihydroxydiphenyldimethyldiarsine (VIII) was obtained.

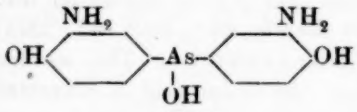


(VII.)

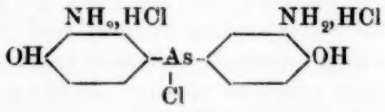


(VIII.)

In the case of 3:3′-dinitro-4:4′-dihydroxydiphenylarsinic acid, complete reduction with sodium hyposulphite leads to 3:3′-*diamino*-4:4′-*dihydroxydiphenylarsenious hydroxide* (IX), for the crude, sparingly soluble reduction product, dissolved in methyl alcohol containing hydrochloric acid and precipitated with concentrated hydrochloric acid, gives rise to 3:3′-*diamino*-4:4′-*dihydroxydiphenylarsenious chloride dihydrochloride* (X), which was obtained in a crystalline condition.



(IX.)

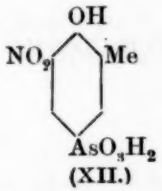


(X.)

If the acid is first reduced to the corresponding *amino-acid* by means of sodium hyposulphite and then completely reduced by means of hypophosphorous acid, 3 : 3′ : 3″ : 3‴-*tetra-amino*-4:4′:4″:4‴-*tetrahydroxytetraphenyldiarsine* (XI) is obtained.

The degree of reduction of the products is readily ascertained by titration with a standard solution of iodine, using starch as indicator, oxidation to the corresponding arsinic acids taking place (compare Gaebel, *Arch. Pharm.*, 1911, **249**, 241).

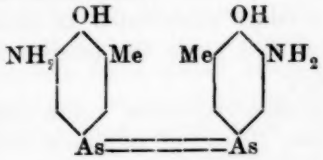
(XI.)



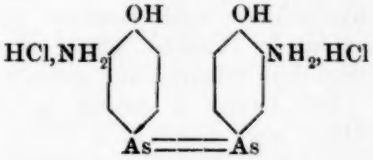
(XII.)

5-Nitro-6-hydroxy-*m*-tolylarsinic acid (XII), first obtained by Benda and Bertheim (*loc. cit.*) by the nitration of 4-hydroxy-*m*-

tolylarsinic acid, can also be prepared from 4-*oxalylamino*-m-*tolylarsinic acid* by the series of reactions outlined above, the preparations from both sources being identical. On reduction with sodium hyposulphite, diaminoarseno-*o*-cresol (4 : 4′-dihydroxy-5 : 5′-diamino-3 : 3′-dimethylarsenobenzene) (XIII) (D.R.-P. 224953) was obtained. This was converted into the *dihydrochloride*, which closely resembles salvarsan (XIV).

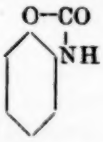


(XIII.)

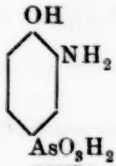


(XIV.)

By the action of carbonyl chloride on *o*-aminophenol, 1 : 2-dihydrobenzoxazolone (XV) is obtained (Schmitt and Henschel, *J. pr. Chem.*, 1888, [ii], **37**, 27; E. von Meyer, *ibid.*, 1915, [ii], **92**, 255). This reaction was applied to 3-amino-4-hydroxyphenylarsinic acid (XVI), giving 1 : 2-*dihydrobenzoxazolone-4-arsinic acid* (XVII), which, on reduction with sodium hyposulphite, yielded the corresponding *arsenobenzene*. It had been hoped that this would prove sufficiently acidic to dissolve in sodium carbonate, but although it dissolves very readily in sodium hydroxide, it is practically insoluble in the carbonate.



(XV.)



(XVI.)

(XVII.)

The estimation of arsenic in organic compounds has been the subject of a recent communication by Ewins (T., 1916, **109**, 1355), who considers that the method devised by Lehmann (*Apoth. Zeit.*, 1912, **27**, 545) for the estimation of arsenic in salvarsan and neosalvarsan, whilst applicable to certain closely allied derivatives, fails entirely in a large number of cases owing to the fact that the preliminary treatment with potassium permanganate and sulphuric acid does not bring about complete oxidation. By a slight alteration of the conditions, it has now been found possible to extend this estimation to a considerable number of substituted phenylarsinic acids containing nitro-, amino-, hydroxy-, methoxy-, bromo-, and other groups, which, by the unmodified method, gave very untrustworthy results owing to incomplete oxidation.

Experimental.

pp′-*Dihydroxydiphenylarsinic Acid* (III).

pp′-Dihydroxydiphenylarsinic acid was obtained by **Benda** (*Ber.*, 1908, **41**, 2371) by diazotising *pp′*-diaminodiphenylarsinic acid in dilute hydrochloric or sulphuric acid, and decomposing the diazo-derivative by passing steam through the solution. Diazotisation in hydrochloric acid, however, gives a product substituted to some extent by chlorine, whilst in sulphuric acid alone the product is very dark-coloured and difficult to purify.

10·5 Grams of sodium *pp′*-diaminodiphenylarsinate, containing $6H_2O$, were dissolved in 75 c.c. of water, 10 c.c. of sulphuric acid added, and diazotised with 50 c.c. of a normal solution of sodium nitrite. The product was mixed with an equal volume of acetic acid to keep the hydroxy-acid produced in solution, and warmed on the water-bath until the elimination of nitrogen had ceased. After boiling with charcoal, the solution was concentrated under diminished pressure, when, on cooling, rather more than 5 grams of the hydroxy-acid separated, whilst the mother liquors yielded further small quantities, the total yield amounting to 75—80 per cent. of the theoretical. The acid is very sparingly soluble in acetone or chloroform, but readily so in methyl alcohol, ethyl alcohol, or 50 per cent. acetic acid, from which it crystallises in plates melting and decomposing at 259° (corr.). (Found: C = 49·0; H = 3·7; As = 25·3. $C_{12}H_{11}O_4As$ requires C = 49·0; H = 3·8; As = 25·5 per cent.)

3:3′-*Dinitro*-4:4′-*dihydroxydiphenylarsinic Acid* (IV).

6·3 Grams of *pp′*-dihydroxydiphenylarsinic acid were dissolved in 35 c.c. of concentrated sulphuric acid and treated gradually with a mixture of 2·5 c.c. of nitric acid (D 1·44) and 2·5 c.c. of sulphuric acid, the temperature being kept at −5° to −3°. After the mixture had remained in a cool place for some time, it was poured on 250 grams of powdered ice, the precipitated acid being collected and washed with water. The yield amounted to 94 per cent. of the theoretical. The acid is almost insoluble in boiling water, fairly readily soluble in glacial acetic acid, and sparingly so in 50 per cent. acetic acid, from which it separates in minute, rhomboidal prisms melting and decomposing at 230° (corr.).

Found: C = 37·5; H = 2·6; N = 7·3; As = 19·6.

$C_{12}H_9O_8N_2As$ (384·1) requires C = 37·5; H = 2·4; N = 7·3; As = 19·5 per cent.

3 : 3′-Diamino-4 : 4′-dihydroxydiphenylarsenious Chloride Dihydrochloride (X).

Two grams of the preceding compound, dissolved in 20 c.c. of water and 5·4 c.c. of 2*N*-sodium hydroxide, were added to a solution of 6 grams of magnesium chloride and 24 grams of sodium hyposulphite in 200 c.c. of water. The resulting solution, which immediately decolorised, was heated to 60° in an atmosphere of carbon dioxide for an hour, a further 10 grams of sodium hyposulphite being added after half an hour. The small quantity of grey powder obtained was dissolved in a little methyl alcohol containing hydrochloric acid, filtered, and added to 100 c.c. of concentrated hydrochloric acid, when a crystalline precipitate gradually separated. This was collected, washed with a few drops of glacial acetic acid and a little ether, and dried in a vacuum over sulphuric acid, the yield amounting to 0·5 gram.

The compound forms glistening leaflets readily soluble in water or methyl alcohol, but sparingly so in concentrated hydrochloric acid. On heating, it darkens above 170° and melts at 215° (corr.).

Found: C = 36·2; H = 3·8; N = 6·9; Cl = 27·0.

$C_{12}H_{12}O_2N_2ClAs,2HCl$ (399·5) requires C = 36·0; H = 3·5; N = 7·0; Cl = 26·7 per cent.

0·1000 Gram required 0·061 gram of iodine for complete oxidation, against 0·063 theoretically required.

3 : 3′-Diamino-4 : 4′-dihydroxydiphenylarsinic Acid and 3 : 3′ : 3″ : 3‴-Tetra-amino-4 : 4′ : 4″ : 4‴-tetrahydroxytetraphenyldiarsine Tetrahydrochloride.

5·1 Grams of 3 : 3′-dinitro-4 : 4′-dihydroxydiphenylarsinic acid were dissolved in 80 c.c. of water and 24 c.c. of 2*N*-sodium hydroxide. The solution, cooled to 0°, was treated in one operation with 17·6 grams of commercial sodium hyposulphite, the temperature rising to about 30°. When the reaction was complete, the solution was cooled, 20 c.c. of 2*N*-hydrochloric acid were added, and as the acid only partly separated, it was salted out by the addition of sodium chloride, and was obtained as a sandy, crystalline precipitate fairly readily soluble in water or methyl alcohol, but sparingly so in ethyl acetate. The yield amounted to 46 per cent. of the theoretical. (Found: N = 8·5. $C_{12}H_{13}O_4N_2As$ (324·1) requires N = 8·6 per cent.)

Two grams of the acid were heated at 60° for one hour in an atmosphere of carbon dioxide with 20 c.c. of hypophosphorous acid

(D 1·15) and a trace of hydriodic acid. As the colourless base obtained by neutralising a test portion of the resulting solution rapidly became purple on exposure, the remainder was added without neutralisation to 150 c.c. of hydrochloric acid. The white precipitate which gradually separated was collected, washed with a few drops of glacial acetic acid and a little dry ether, and dried in a vacuum. The product is readily soluble in water or methyl alcohol.

Found: N = 7·6; Cl = 19·7.

$C_{24}H_{24}O_4N_4As_2,4HCl$ (728·1) requires N = 7·7; Cl = 19·5 per cent.

0·1001 Gram required 0·103 gram of iodine for complete oxidation, as against 0·104 gram theoretically required.

pp′-*Dioxalylaminodiphenylarsinic Acid* (V).

When oxalic acid is allowed to react with *pp′*-diaminodiphenylarsinic acid at a temperature approaching 160°, some fission of the molecule results, so that a mixture is obtained from which the desired product can be isolated by taking advantage of the sparing solubility of its barium salt in cold dilute ammonia, the barium salt of *p*-aminophenylarsinic acid being precipitated only on boiling.

8·4 Grams of sodium *pp′*-diaminodiphenylarsinate containing $6H_2O$ were intimately mixed with 15·1 grams of oxalic acid and heated in an oil-bath with constant stirring at 140° until most of the water had disappeared, and then to 160° until quite hard. The product was well ground with 80 c.c. of water and 8 c.c. of hydrochloric acid, collected, and well washed with water. It was then dissolved in ammonia and treated with a cold solution of barium chloride. The resulting precipitate was collected, well washed with water, and decomposed by grinding with dilute hydrochloric acid. A small quantity which remained in the acid was precipitated on dilution. pp′-*Dioxalylaminodiphenylarsinic acid* is only sparingly soluble in boiling water, alcohol, or methyl alcohol, and practically insoluble in benzene, ether, or ethyl acetate. It is more readily soluble in acetic acid or 50 per cent. acetic acid, and crystallises in slender needles which contain $4H_2O$.

Found: loss at 110° = 13·8.

$C_{16}H_{13}O_8N_2As,4H_2O$ requires 14·1 per cent.

In material dried at 110°, C = 44·1; H = 3·3; N = 6·4.

$C_{16}H_{13}O_8N_2As$ (436·2) requires C = 44·0; H = 3·0; N = 6·4 per cent.

Nitration with a mixture of nitric and sulphuric acids, and subsequent acid hydrolysis, led to the formation of 3:3′-*dinitro*-4:4′-

diaminodiphenylarsinic acid (VI), a yellow, crystalline powder very sparingly soluble in water and the usual organic solvents.

Found: N = 14·3.

$C_{12}H_{11}O_6N_4As$ (382·1) requires N = 14·7 per cent.

This was converted by warming with an excess of potassium hydroxide solution into 3:3′-dinitro-4:4′-dihydroxydiphenylarsinic acid, identical with that described above.

6-*Oxalylamino*-m-*tolylarsinic Acid.*

Five grams of sodium 6-amino-*m*-tolylarsinate (containing $3H_2O$) and 6 grams of oxalic acid were intimately mixed and heated first at 140° until most of the water had been driven off, and then at 160° until quite dry. The residue was triturated with 50 c.c. of water and 7 c.c. of hydrochloric acid, collected, and washed with water. The product, which was anhydrous, amounted to rather more than 3 grams. It was found to be sparingly soluble in hot alcohol, ethyl acetate, or acetone, more readily so in hot water, and readily so in 50 per cent. acetic acid, from which it crystallised in elongated, rhombic prisms.

Found: N = 4·5; As = 24·6.

$C_9H_{10}O_6NAs$ (303·1) requires N = 4·6; As = 24·7 per cent.

5-*Nitro*-6-*amino*-m-*tolylarsinic Acid.*

Six grams of the above oxalyl derivative were dissolved in 20 c.c. of sulphuric acid, and a mixture of 1·2 c.c. of nitric acid (D 1·4) and 1·2 c.c. of sulphuric acid was gradually added below 15°. When the reaction was complete, the product was poured into 100 c.c. of water, boiled under a reflux condenser for two hours, cooled, and the acid which separated, amounting to 4·6 grams, collected. 5-*Nitro*-6-*amino*-m-*tolylarsinic acid* is fairly readily soluble in boiling water, from which it separates in slender needles consisting of a mixture of the yellow anhydrous form and the orange hydrated form. It gradually passes completely into the latter, which contains $1\frac{1}{2}H_2O$.

Found: loss at 110° = 9·3.

$C_7H_9O_5N_2As,1\frac{1}{2}H_2O$ requires H_2O = 9·0 per cent.

In dried substance, N = 9·9.

$C_7H_9O_5N_2As$ (276·1) requires N = 10·1 per cent.

*5-Nitro-6-hydroxy-*m*-tolylarsinic Acid* (XII).

Two grams of the acid just described were heated on the water-bath with 10 c.c. of 40 per cent. potassium hydroxide solution until a test portion no longer showed the presence of an amino-group. The product was then cooled and acidified with hydrochloric acid, giving almost the theoretical yield of 5-nitro-6-hydroxy-*m*-tolylarsinic acid. This was compared with a specimen prepared by Benda and Bertheim's method (*Ber.*, 1911, **44**, 3445), and found to be identical with it. Both products, when crystallised rapidly from boiling water, formed clusters of slender, yellow needles, and when crystallised slowly from 50 per cent. acetic acid, well-defined, rhombic prisms. When heated in the same bath, both products decomposed explosively at 310°, whilst the mixture of the two behaved identically.

The *acetyl* derivative, prepared by the action of acetic anhydride in the presence of a trace of pyridine, is fairly readily soluble in methyl or ethyl alcohol or boiling water, but sparingly so in cold water or ethyl acetate. When crystallised from water, it forms colourless, spherical nodules, which are anhydrous.

Found: N = 4·4.

$C_9H_{10}O_7NAs$ (319·1) requires N = 4·4 per cent.

4:4′-Dihydroxy-5:5′-diamino-3:3′-dimethylarsenobenzene Dihydrochloride.

The reduction of the 5-nitro-6-hydroxy-*m*-tolylarsinic acid was effected by means of sodium hyposulphite under the conditions described by Ehrlich and Bertheim (*Ber.*, 1912, **45**, 757; compare D.R.-P. 224953). The dihydrochloride, which was obtained in a yield of 70 per cent. of the theoretical, formed a pale yellow, microcrystalline powder readily soluble in water or methyl alcohol, much less readily so in ethyl alcohol, and practically insoluble in ether or acetone.

Found: Cl = 13·6; As = 29·9.

$C_{14}H_{16}O_2N_2As_2,2HCl,2H_2O$ (503·1) requires Cl = 14·1; As = 29·8 per cent.

3-Amino-4-hydroxyphenylarsinic Acid.

The reduction of nitrohydroxyphenylarsinic acid to the corresponding amino-acid by means of sodium hyposulphite has been

described in D.R.-P. 224953. The following modification of the method gives excellent results.

Twenty-six grams of 3-nitro-4-hydroxyphenylarsinic acid were dissolved in 200 c.c. of *N*-sodium hydroxide, cooled to −2°, and to the well-stirred solution 65 grams of sodium hyposulphite (80 per cent.) were added in one operation. The colour of the solution disappeared at once, and the temperature rose to 25°, whilst the amino-acid commenced to deposit. The precipitation was completed by the addition of 23 c.c. of hydrochloric acid (D 1·12). The acid was collected and well washed with water; the yield in several experiments ranged between 65 and 80 per cent. of the theoretical.

1 : 2-*Dihydrobenzoxazolone-4-arsinic Acid* (XVII).

A solution of 11·6 grams of aminohydroxyphenylarsinic acid in 150 c.c. of 5 per cent. sodium hydroxide, cooled by ice and stirred vigorously, was gradually treated with 110 c.c. of a 6·5 per cent. solution of carbonyl chloride in toluene. At the conclusion of the reaction, the two layers were separated, the aqueous layer being extracted with ether and then acidified with hydrochloric acid, when the oxazolone separated as a sandy, crystalline precipitate in a yield amounting to 83 per cent. of the theoretical.

It is sparingly soluble in alcohol, but readily so in boiling water, from which it separates in colourless, prismatic needles which are anhydrous. On heating, it rapidly decomposes above 250° without melting.

Found: C = 32·5; H = 2·5; N = 5·4; As = 28·6.
$C_7H_6O_5NAs$ (259·0) requires C = 32·4; H = 2·3; N = 5·4; As = 28·9 per cent.

1 : 2 : 1′ : 2′-*Tetrahydro-4-arsenobenzodioxazolone.*

2·3 Grams of 1 : 2-dihydrobenzoxazolone-4-arsinic acid were dissolved in a mixture of 50 c.c. of water and 8 c.c. of 2*N*-sodium hydroxide, added to a solution of 15 grams of sodium hyposulphite and 3 grams of magnesium chloride in 70 c.c. of water, and heated, with stirring, for an hour at 60° in an atmosphere of carbon dioxide. A yellow, granular precipitate gradually formed, which, after cooling, was collected and well washed with water. A portion was dried to constant weight in a vacuum over sulphuric acid, and formed a pale yellow, granular powder insoluble in water or the usual organic solvents or in sodium carbonate, but readily soluble in aqueous sodium hydroxide.

Found: N = 6·5; As = 35·6.

$C_{14}H_8O_4N_2As_2$ (418·1) requires N = 6·7; As = 35·9 per cent.

The remainder was dissolved in aqueous sodium hydroxide, and the *sodium* salt precipitated by the addition of alcohol. This, after drying in a vacuum, was obtained as a pale yellow, fairly stable powder readily soluble in water, sparingly so in alcohol, and insoluble in ether.

Estimation of Arsenic in Substituted Phenylarsinic Acids.

For the estimation of arsenic in the foregoing and many other compounds, the following modification of Lehmann's method (*Apoth. Zeit.*, 1912, **27**, 545) has been used, and has been found to give good results generally with substituted phenylarsinic acids.

0·2 Gram of the powdered substance is accurately weighed and intimately mixed in a 250 c.c. flask with 1 gram of potassium permanganate. Five c.c. of 50 per cent. sulphuric acid are added, followed by a further 10 c.c. of concentrated sulphuric acid when the first reaction has ended. After a few minutes, 10 c.c. of water are added, and the mixture is heated for half an hour to gentle boiling, precautions being taken against loss by spraying. The manganese dioxide is then removed by a slight excess of hydrogen peroxide, 30 c.c. of water are added, and the solution is again boiled for ten minutes, after which a dilute solution of potassium permanganate is added drop by drop until a faint, permanent pink tinge is obtained. This is discharged by the addition of a drop of a dilute solution of oxalic acid. The solution is then cooled, 2·5 grams of potassium iodide are added, the whole being allowed to remain for an hour, and the liberated iodine titrated by means of thiosulphate. A blank experiment should be carried out alongside each estimation, and the final reading corrected accordingly.

The following are examples of the results obtained:

Substance.	As	
	Found.	Calc.
3-Nitro-4-hydroxyphenylarsinic acid	28·4, 28·4	28·5
p-Aminophenylarsinic acid	34·5, 34·5	34·6
1 : 2-Dihydrobenzoxazolone-4-arsinic acid	28·6	28·9
3-Nitro-4-aminophenylarsinic acid	28·9, 28·8	28·6
3 : 3′-Dinitro-4 : 4′-dihydroxydiphenylarsinic acid	19·6, 19·5	19·5
p-Bromophenylarsinic acid	26·5	26·7

In conclusion, the author desires to express his thanks to Professor F. L. Pyman for his interest during the course of the investigation.

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LXXXIV.—*The Selective Combustion of Carbon Monoxide in Hydrogen.*

By Eric Keightley Rideal.

In a recent communication (*Analyst*, 1919, **44**, 89), it was shown that small quantities of carbon monoxide in hydrogen could be preferentially oxidised to carbon dioxide by passing the gaseous mixture admixed with a small quantity of oxygen over certain catalytic materials maintained at suitable temperatures.

The following conclusions were drawn, namely, that the preferential nature of the combustion was affected by the nature and temperature of the catalyst employed; thus, the oxides of copper (operative at 110°) and of iron and chromium (operative at 250° to 350°) were extremely efficacious in inducing the combustion of the carbon monoxide, whilst an enhanced activity could be obtained by the addition of certain promoters, such as ceria and thoria, in small quantities to the mixed oxides. With reduced nickel, on the other hand, complete interaction of oxygen and the hydrogen was obtained. At the time, it was considered probable that with suitable catalytic material maintained at the proper temperatures only carbon monoxide, and no hydrogen, could be burnt, the selective nature of the reaction being gradually lost with elevation of the temperature. It was also established that complete elimination of the carbon monoxide could be effected by this means, and that the mechanism was not founded on the operation of the water-gas reaction, $H_2O + CO \rightleftharpoons H_2 + CO_2$, at low temperatures.

In view of the importance of the processes of selective combustion, such as of hydrogen sulphide in hydrogen, phosphine in ammonia, which are being investigated, and of the present example, it was deemed of interest to study the mechanism of the reaction in somewhat greater detail in order, if possible, to obtain material to assist in making a decision as to the validity of the various theories of heterogeneous catalysis which are now extant. In the case of the catalytic combination of hydrogen and oxygen on the surface of platinum black, the theory of an intermediate compound is strongly supported by the work of Engler and Wöhler (*Zeitsch. anorg. Chem.*, 1901, **29**, 1; *Ber.*, 1903, **36**, 2642), whilst Sabatier, in his researches on hydrogenation by means of metallic nickel, concluded that his results were explicable on the assumption that an unstable nickel hydride was formed ("La Catalyse en Chimie Organique").

Faraday (*Phil. Trans.*, 1834, **114**, 55), on the other hand, gave ardent support to the adsorption theory. Recently, Bancroft (*J. Physical Chem.*, 1917, **21**, 8), from a survey of the work of Turner, Henry, Lunge, Harbeck, and Bone, draws the conclusion that the facts are capable of the simplest explanation on the adsorption theory.

The adsorption theory, however, is capable of several interpretations, which at the present time are developing along two distinct lines, that may be termed the *diffusion theory* and the *single layer theory*. In the diffusion theory, which finds its expression in the work of Bodenstein (*Zeitsch. physikal. Chem.*, 1899, **29**, 655, *et seq.*), and for which some support can be gained from the experiments of Bone and his co-workers (*Phil. Trans.*, 1906, [*A*], **206**, 1), the adsorbed layer is relatively thick and the velocity of reaction is governed rather by the rate of diffusion of the reactants and products in this layer than by the rate of chemical change occurring at the actual surface of the catalyst. In the single layer theory, advanced by Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2221; 1917, **39**, 1848; 1918, **40**, 1361), Harkins (*ibid.*, 1917, **39**, 591), and Marcelin, the surface film is considered to be only one molecule thick, thus showing an abrupt change in continuity, and the reactions take place in that surface skin. Lewis (this vol., p. 182) has recently applied the radiation hypothesis to explain the enhanced reaction velocities obtained in the presence of heterogeneous catalytic materials, and has adopted the "single layer" theory as "the most probable material mechanism of the process considered." A summary of the results of Bodenstein and Bone and Wheeler on the catalytic combination of hydrogen and oxygen is likewise given in this paper. Bodenstein and Ohmer's investigations (*Zeitsch. physikal. Chem.*, 1905, **53**, 166) on the catalytic combination of carbon monoxide and oxygen on the surface of hot quartz between 300° and 570° led them to the conclusion that the rate of combination was proportional to the partial pressure of the oxygen and inversely proportional to the concentration of carbon monoxide, a case of negative catalysis; estimations were carried out by the manometric method.

Experimental.

The catalytic materials investigated were prepared as follows:

Iron oxide, prepared by the gentle ignition of the nitrate, the remainder of the oxides of nitrogen being expelled by heating in a current of steam at 400°. The coarse lumps obtained in this way were broken up, and uniform pieces, some 0·2 cm. in diameter, utilised for experimental purposes.

Iron oxide containing 2·5 per cent. of chromium oxide and 0·5 per cent. of cerium oxide, prepared in a similar manner from the nitrates of iron and cerium with the admixture of the chromium salt in the form of ammonium dichromate.

Copper oxide prepared from copper wire by alternate oxidation and reduction with air and hydrogen respectively. The gases were carefully freed from any possible contamination with hydrogen sulphide or sulphur dioxide. The copper oxide was considered sufficiently active when appreciable quantities of water were formed when hydrogen was passed over it at 120°.

Nickel prepared by soaking small pieces of diatomite in nickel nitrate, followed by gentle ignition and heating in superheated steam. The finished product contained 5 per cent. of nickel.

Palladium.—An ordinary purchased sample of good quality palladised asbestos was used for this purpose.

Preliminary experiments having shown that it was extremely difficult to prepare two specimens of catalytic material identical in activity, and, further, that the activity of the catalyst underwent marked fluctuations in the course of an experiment, first increasing and then decreasing, it was decided not to attempt to measure the relative velocities of catalytic combustion of hydrogen and carbon monoxide in separate experiments, but to determine the relative rates of combustion of these constituents in gas mixtures containing hydrogen, oxygen, and carbon monoxide.

The gas mixtures of various compositions were obtained from electrolytic hydrogen and oxygen and carbon monoxide produced from oxalic and sulphuric acids, the carbon dioxide being removed by means of sodium hydroxide. Prior to use, the gas mixture was carefully freed from any traces of carbon dioxide and from moisture by means of soda-lime and phosphoric oxide.

The furnace was similar to that employed in the analytical instrument previously mentioned, but was constructed throughout of silica instead of glass. It consisted essentially of two co-axial silica tubes, the outer one electrically heated and so arranged that the gases could pass in through the annular space between the tubes and down through the catalyst in the central tube. In this way, uniformity of temperature in the catalyst was ensured.

In each experiment, 5 c.c. of catalyst were employed; no attempt was made to approximate to the same superficial area of catalytic material, although experiments have shown that with a uniform catalytic material the activity is proportional to the superficial area of the grains; this generalisation, however, does not apply to fine powders or to relatively large pieces of porous materials.

A series of experiments was conducted by passing the gas mixture through the catalytic material maintained at suitable tempera-

tures, and determining the quantities of water and carbon dioxide formed by the usual methods adopted in processes of organic combustion, namely, absorption and weighing. In all cases, the temperature was accurately controlled by means of a thermometer, around the bulb of which the catalytic material was built up, and care was taken to ensure passage of the gas mixture through the furnace at such a rate that the fractional conversion was but small. This consideration is of some importance in the light of the diffusion theory, for if we imagine the surface of the catalyst to be covered with a small atmosphere of the products of the reaction, carbon dioxide and steam, then, if the gas is quiescent, fresh reactants can only approach the catalyst by diffusion, and the atmosphere will slowly extend from the surface of the catalyst to the walls of the containing vessel. Under these conditions, the phenomenon of catalysis is not being observed, but there are recorded merely some rates of diffusion liable to large errors caused by convection, especially if the reaction is strongly exothermic. A gentle movement of the gas will consequently upset these conditions, and the rates of reaction will be affected by the nature and magnitude of this movement.

This does not necessarily preclude the diffusion theory of catalysis, since in this case it is assumed that the atmosphere round the catalyst is maintained by the molecular forces of the material, and that the "diffusion layer," as in the case of liquid and solid surfaces investigated by Noyes and Whitney (*Zeitsch. physikal. Chem.*, 1897, **23**, 689), is relatively thin—of the order of 0·05 to 0·1 mm. It will therefore suffice always to maintain the gas velocity past the catalyst grains, so that the "diffusion layer," if it exists at all, will not exceed the normal thickness produced by adsorption. On the other hand, the velocity of the flow of gas must not be raised too high, since evidence is not lacking in the possibly analogous case of liquid and solid surfaces that the adsorption film is affected by high velocities; thus, A. Fischer and the author computed that the thickness of the film was reduced from 0·0635 mm. to 0·0510 mm. by agitating the liquid by means of a stirrer rotating at 250 and 1100 revolutions per minute respectively.

In the first series of experiments, a mixture containing approximately 10 per cent. of carbon monoxide, 10 per cent. of oxygen, and 80 per cent. of hydrogen was passed through the various catalytic materials at various temperatures from 150° to 380°. Below 150°, the activity of all the catalysts employed, with the exception of palladium, was too slight to yield trustworthy results, and at high temperatures the activity became so great that, in spite of reducing

the quantity of catalyst in the furnace and considerably augmenting the velocity of the gas, a very considerable conversion of the reactants took place, which, for the reasons already stated, was undesirable.

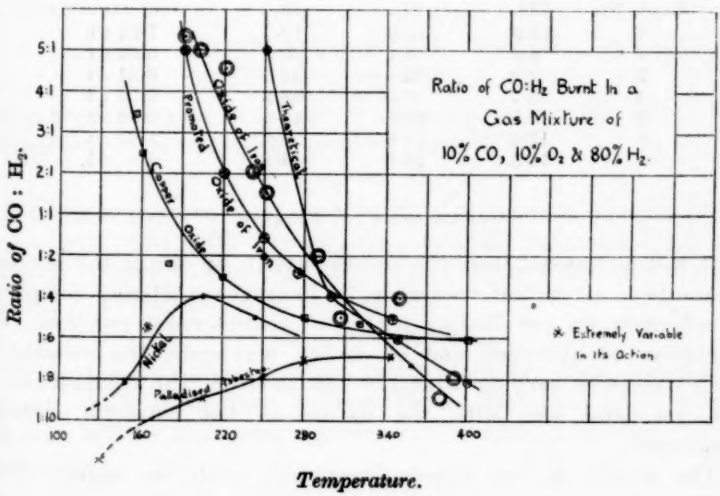
The results of these experiments are shown in the attached curves, from which the two following typical examples may be cited:

Catalyst, iron oxide.

Temperature, 220°.

Composition of gas: CO = 9; O_2 = 14; H_2 = 77 per cent.

Vol. of gas used. Litres.	Time in hours.	Weight of H_2O collected.	Weight of CO_2 collected.	Ratio vol. CO : H_2 burnt.
0·768	1·5	0·0121	0·1332	4·43 : 1
0·568	1·75	0·0092	0·0964	4·22 : 1
0·424	2·0	0·0062	0·0702	4·28 : 1
			Mean.....	4·32 : 1



Catalyst, copper oxide.

Temperature, 280°.

Composition of gas: CO = 14; O_2 = 11·5; H_2 = 74·5 per cent.

Vol. of gas used. Litres.	Time in hours.	Weight of H_2O collected.	Weight of CO_2 collected.	Ratio vol. CO : H_2 burnt.
1	0·5	0·0442	0·0508	0·470 : 1
1	0·5	0·0298	0·0344	0·472 : 1
1	0·5	0·0390	0·0431	0·452 : 1
			Mean.....	0·466 : 1

In all cases, the interesting observation was made that a catalyst which had been allowed to cool exposed to the air, liberated first, on warming in the stream of gas, a relatively large quantity of carbon dioxide, and, at higher temperatures, water vapour; further, on raising the temperature of a catalyst in the mixture of gases, the ratio $CO : H_2$ burnt, as obtained by estimation of the water and carbon dioxide, during the first twenty minutes or so, fell short of the ratio when constant velocity ratios were obtained.

In the second series of experiments, only one catalytic material was employed, namely, iron oxide, and the gaseous mixture was altered in composition in order to determine the effect of an alteration in the partial pressures of the reactants on the relative rates of reaction.

In these experiments, the temperature of the catalyst was maintained at 220°, when the following ratios were obtained:

	Composition of gas per cent.			Ratio $CO : H_2$ by volume burnt. Mean of several experiments.
Expt. No.	CO.	O_2.	H_2	
1	12·3	10·0	77·7	1·24 : 1
2	4·6	5·1	90·3	0·54 : 1
3	2·3	5·5	42·7	0·21 : 1
4	5·7	7·0	88·3	0·52 : 1
5	2·5	39·0	48·5	0·30 : 1
6	12·0	12·6	75·4	1·25 : 1
7	16·6	19·2	64·2	1·6 : 1

Discussion of Results.

It will be noticed from the curves that in no case is the selective combustion of carbon monoxide in hydrogen perfectly complete; in all cases we are dealing with two simultaneous reactions, the oxidation of hydrogen and of carbon monoxide, the velocity of each naturally varying with the temperature, the composition of the gas, and also with the nature of the catalytic material employed.

The results do not appear compatible with the theory of an intermediate compound as interpreted in the older sense and not on Langmuir's view of surface combination, since no evidence of stable hydrides or carbonyls was obtained. The results, in addition, do not favour the adsorption theory of catalysis, for the following reasons.

Assuming that the reaction velocity is governed entirely by the rate of diffusion of the reactants through the atmosphere of carbon dioxide and steam around the material, then the relative reaction velocities, at any definite temperature, should not change to any marked extent with the nature of the catalytic material employed,

and, further, owing to the greater mobility of hydrogen, this gas should burn more quickly than carbon monoxide, especially at relatively low temperatures, when the adsorbed atmosphere is presumably denser than at more elevated temperatures. Neither of these deductions is confirmed by the experimental figures.

The general shape of the temperature : ratio curves obtained can, however, be deduced from theoretical considerations if Langmuir's theory of single layer absorption is adopted, together with Lewis's application of the Marcelin-Rice principle of activation to heterogeneous systems.

It is evident that the dependence of the ratio $CO : H_2$ burnt, on the partial pressure of the reactants on a given catalyst at a definite temperature, indicates the relative reaction velocities of two separate reactions, the surface oxidation of hydrogen and of carbon monoxide; these can be expressed in the form:

$$\begin{aligned}
\text{I}\quad &(a)\ 2H_2 + O_2 \longrightarrow 2H_2O \\
&(b)\ H_2 + O_2 \longrightarrow H_2O_2 \longrightarrow H_2O \\
\text{II}\quad &(a)\ 2CO + O_2 \longrightarrow 2CO_2 \\
&(b)\ CO + O_2 \longrightarrow CO_3 \longrightarrow CO_2 \\
&(c)\ CO + \tfrac{1}{2}O_2 \longrightarrow CO_2
\end{aligned}$$

Lewis gives evidence in favour of assuming that in the case of the combustion of hydrogen the primary reaction is

$$H_2 + O_2 \longrightarrow H_2O_2,$$

supported to some extent by the work of Bone and Wheeler (*Phil. Trans.*, 1906, [*A*], **206**, 1), who disagree with Bodenstein (*Zeitsch. physikal. Chem.*, 1899, **29**, 665), whose figures for the velocity constant corresponded with the reaction

$$2H_2 + O_2 = 2H_2O.$$

In the present instance, where ratios alone are being considered, we can easily distinguish between these reactions, since if each reaction follows the same course, for example. I (*a*) and II (*a*), then, since

$$2H_2 + O_2 = 2H_2O$$
$$2CO + O_2 = 2CO_2$$

$$-\frac{dc_{H_2}}{dt} = (H_2)^2(O_2)$$

and

$$-\frac{dc_{CO}}{dt} = (CO)^2(O_2)$$

or

$$\frac{-\dfrac{dc_{CO}}{dt}}{-\dfrac{dc_{H_2}}{dt}} = \frac{(CO)^2}{(H_2)^2},$$

that is, the relative velocities of combustion are independent of the concentration of oxygen.

If, on the other hand, the oxidation of hydrogen and carbon monoxide proceeds differently, say according to the equations I (b) and II (c), then, since

$$H_2 + O_2 \longrightarrow H_2O_2 \longrightarrow H_2O$$
$$CO + \tfrac{1}{2}O_2 \longrightarrow CO$$

$$\frac{-\frac{dc_{CO}}{dt}}{-\frac{dc_{H_2}}{dt}} = \frac{(CO)(O_2)^{\frac{1}{2}}}{(H_2)(O_2)} = \frac{(CO)}{(H_2)(O_2)^{\frac{1}{2}}},$$

that is, the relative rates will be a function of the pressure of oxygen. From the above experimental determinations, all the possible ratios can be calculated. A few trials were sufficient to indicate that one ratio, and one ratio only, gave figures closely approximating to those experimentally determined, namely,

$$\frac{-\frac{dc_{CO}}{dt}}{-\frac{dc_{H_2}}{dt}} = \frac{(CO)}{(H_2)(O_2)^{\frac{1}{2}}}$$

and the experimental and calculated values are given in the following table:

Expt. No.	Ratio: $\frac{CO : H_2 \text{ (Expt. I.)}}{CO : H_2 \text{ (Expt. II.)}}$ of gases burnt.	Ratio: $\frac{\frac{(CO)}{(H_2)(O_2)^{\frac{1}{2}}} \text{ (Expt. I.)}}{\frac{CO}{(H_2)(O_2)^{\frac{1}{2}}} \text{ (Expt. II.)}}$ calculated from compositions of mixtures.
1		
2	2·3	2·28
3	2·6	3·0
4	0·40	0·30
5	1·7	2·9
6	0·24	0·19
7	0·77	0·76

It will be observed that, with the exception of the ratio expt. 4 : 5, the agreement is fairly good between the observed figures and those calculated on the assumption that the velocities of reaction are in accordance with one of the two following schemes:

A. $\left\{\begin{array}{l} H_2 + O_2 \longrightarrow H_2O_2 \longrightarrow H_2O \\ CO + \tfrac{1}{2}(O_2) \longrightarrow CO_2 \end{array}\right.$

B. $\left\{\begin{array}{l} H_2 + \tfrac{1}{2}(O_2) \longrightarrow H_2O \\ \text{CO rate independent of the concentration of oxygen.} \end{array}\right.$

Although from these experiments it is impossible to distinguish between these two hypothetical cases, yet, in view of the fact that carbon monoxide is burnt on all the catalysts investigated, whether

oxides or not, it may be assumed that the first set of reactions is probably more correct, which on Langmuir's hypothesis would indicate that the hydrogen and carbon monoxide were bound by only one valency bond to the catalytic material, and the oxygen both by one and by two.

Lewis adopts the hypothesis that the oxygen is adsorbed by the catalyst and exists in the atomic state on its surface, and that all that is necessary is for an activated molecule of hydrogen or carbon monoxide to come into contact with an atom of oxygen. If we adopt the hypothesis that the number of active oxygen atoms or molecules are already present in large excess, and that the reaction velocity is governed entirely by the number of molecules of hydrogen or carbon monoxide that receive the necessary critical energy increment per second, then the ratio of gases burnt should be independent of the concentration of oxygen, which is not the case. It would appear, however, that the energy necessary to activate a gram-molecule of oxygen sufficiently for it to become reactive at the surface of such catalysts is extremely small, and for the purposes of calculation may be neglected.

The reaction velocity of each reaction is accordingly given by the expressions

$$-\frac{dc_{CO}}{dt} = ae^{-\frac{(Nh\nu_{CO} + L_{CO_2})}{RT}}$$

$$-\frac{dc_{H_2}}{dt} = a'e^{-\frac{(Nh\nu_{H_2} + L_{H_2O})}{RT}}$$

or

$$\frac{-\frac{dc_{CO}}{dt}}{-\frac{dc_{H_2}}{dt}} = \frac{a}{a'}\, e^{\frac{Nh\nu_H - Nh\nu_{CO} + L_{H_2O} - L_{CO_2}}{RT}}$$

where ν_{CO}, ν_{H_2} are the frequencies of the radiation bringing about the partial activation of hydrogen and carbon monoxide, N the number of molecules per gram-molecule, h Planck's constant, L_{H_2O} and L_{CO_2} the heat of desorption per gram-molecule of the products of the reaction, namely, water and carbon dioxide at the temperature T, $\frac{a}{a'}$ the ratio of the surface concentrations of carbon monoxide and hydrogen. For the purposes of calculation, L_{H_2O} and L_{CO_2} are taken as the latent heats of water and carbon dioxide at the respective temperatures, it being assumed that the values alter in a linear manner with the temperature. For water, the values adopted are 9000 calories at 100° and 0 at 365°, the critical

point; for carbon dioxide, 6200 calories at 0° and 0 at 35°. Lewis's value, deduced from Bohr's atomic model of 21,000 calories per gram-molecule, is taken as the experimental value of $Nh\nu_{H_2}$, whilst that for carbon monoxide was calculated as follows. Assuming the equality of the four carbon linkings in the carbon atom, then from the heats of combustion of carbon and its oxide:

$$C + O_2 = CO_2 + 94{,}320$$
$$CO + O = CO_2 + 68{,}220$$
Therefore $$C + O = CO + 26{,}100,$$

or the heat equivalent of two carbon–oxygen linkings is

$$68{,}220 - 26{,}100 = 42{,}120 \text{ calories},$$

or 21,060 for one valency.

If we assume that the carbon monoxide is activated by desorption after adsorption on to the oxide catalyst by means of one carbon–oxygen valency, the necessary critical increment for such an activation is 21,060 calories per gram-molecule, or

$$Nh\nu_{CO} = 21{,}060.$$

Therefore $Nh\nu_{H_2} - Nh\nu_{CO} = -60$ calories only, or the spectral regions in which hydrogen and carbon monoxide are activated are practically identical. An approximately similar result may be obtained from the ionising potentials of the two gases. It can easily be shown that the critical increment $Nh\nu$ is equal to $2{\cdot}2 \times 10^4 V$ (where V is the ionising potential in volts). The value of V for hydrogen is approximately 16 and for carbon monoxide about 15·8 to 15·9 volts; thus, in this case, $Nh\nu_{H_2} - Nh\nu_{CO} = +3000$ calories. These figures are necessarily somewhat inexact, and the degree of activation required for catalytic chemical reaction is probably much less than is required for ionisation, as indicated by the above figures.

The following table summarises the results of the calculation for the determination of the ratio of the reaction velocities at various temperatures, on the assumption that the activation of the oxygen is not a part of the process.

Temperature.	L_{H_2O}.	L_{CO_2}.	$\frac{-60+L_{H_2O}-L_{CO_2}}{RT}$.	$e^{\frac{-60+L_{H_2O}-L_{CO_2}}{RT}}$.
− 50°	14,500	18,000	− 9·0	0·0001
0	12,500	6,000	11·8	135,000
50	10,800	0	16·6	16×10^6
100	9,000	—	12·0	205,000
200	5,500	—	5·7	300
250	3,900	—	3·7	40·5
300	2,000	—	1·7	5·5
350	500	—	0·35	1·42
400	0	—	−0·04	0·96

The relative velocities of combustion for a mixture of carbon monoxide and hydrogen in the ratio of 1:8, calculated from the above table, are shown in the curve, and the similarity in form between this derived curve and that experimentally determined on the iron oxide catalyst is clearly indicated. A closer agreement is scarcely to be expected, since the factor introduced by the possible activation of the oxygen and the effect of its partial pressure on the reaction velocity have been neglected, together with the uncertainty introduced by equating the latent heat with the heat of desorption. It follows that the removal of carbon monoxide from hydrogen by this means takes place most readily at about 50° to 100°, whilst below −50° and above 400° hydrogen burns more quickly than carbon monoxide, selective combustion being entirely dependent on the fact that energy is required for the desorption of one of the products of combustion, namely, water vapour, although in the case of iron oxide it is scarcely sufficiently reactive below 220° to permit of the optimum conditions of operation.

It is interesting to note that at high temperatures hydrogen burns more quickly than carbon monoxide.

It is evident that the simple adsorption theory, where the hydrogen and carbon monoxide are adsorbed and activated by radiation and the oxygen is adsorbed and activated by the catalyst, gives an adequate explanation for the observed dependence of the reaction velocity ratios on the composition of the gas and on the influence of temperature, but these considerations do not give any insight into the dependence of the ratio on the composition of the catalyst.

The temperature-coefficients of both these reactions are sufficiently large to exclude the hypothesis that every hydrogen and carbon monoxide molecule striking the surface and becoming attached to the catalyst is oxidised; one is forced to assume that the ratio $\frac{a}{a'}$, which is the ratio of the surface concentrations of the two gases, varies with the catalytic material. Adopting the hypothesis of molecular attachment by one bond for hydrogen and carbon monoxide, the ratio of the surface concentrations can be derived by Langmuir's equation:

$$\frac{N}{N_0}\alpha = \frac{\sigma\mu}{1+\sigma\mu}$$

where N = Avogadro's constant.

N_0 = number of space lattices per sq. cm.

$\sigma = \frac{A}{V}$, where V = rate of evaporation from a completely

covered surface; A, a factor approximating to unity, being the fraction of the number of molecules striking the surface which are absorbed.

$\mu =$ gram-molecules striking.

$= K\dfrac{P}{\sqrt{MT}}$, where P is the gas pressure, M the molecular weight, and T the absolute temperature.

$\alpha =$ gram-molecules adsorbed per unit area.

Hence

$$\frac{a_{CO}}{a_{H_2}} = \frac{\sigma_1\mu_1(1+\sigma_2\mu_2)}{\sigma_2\mu_2(1+\sigma_1\mu_1)} = \frac{P_{CO}A_{CO}(V_{H_2}\sqrt{M_{H_2}T}+A_{H_2}P_{H_2})}{P_{H_2}A_{H_2}(V_{CO}\sqrt{M_{CO}T}+A_{CO}P_{CO})}.$$

Putting $A_{CO}=A_{H_2}$,

$$\frac{a_{CO}}{a_{H_2}} = \frac{P_{CO}(V_{H_2}\sqrt{M_{H_2}T}+AP_{H_2})}{P_{H_2}(V_{CO}\sqrt{M_{CO}T}+AP_{CO})},$$

whilst if each molecule is attached by two bonds,

$$\frac{a_{CO}}{a_{H_2}} = \frac{\sqrt{\sigma_1\mu_1}}{\sqrt{\sigma_2\mu_2}} = \sqrt{\frac{V_{H_2}P_{CO}\sqrt{M_{H_2}}}{V_{CO}.P_{H_2}\sqrt{M_{CO}}}}.$$

We have assumed in the former calculation that the surface concentration ratio $\frac{a}{a'}$ is equal to the ratio

$$K\,\frac{P_{CO}}{P_{H_2}}.\frac{V_{H_2}}{V_{CO}}$$

(where K is a constant), which is actually the case for any one particular catalytic material, but a closer approximation is given by

$$\frac{a}{a'} = K\frac{P_{CO}}{P_{H_2}}.\frac{V_{H_2}}{V_{CO}},$$

where V_{H_2} is the rate of evaporation of hydrogen from a completely covered surface. In the cases considered, where we are dealing with the evaporation of a gas from a solid surface, the rate of evaporation from a completely covered surface may be regarded as a simple function of the vapour pressure. It follows that for various surfaces the rates of evaporation of gases are not the same, and we must postulate, as Langmuir has done, quasi-chemical combination between gas and surface, these quasi-chemical combinations possessing different free energies. Since little is known about the unstable hydrides of the elements, the work of Sieverts (*Zeitsch. physikal. Chem.*, 1907, **60**, 169, *et seq.*; see

also D. P. Smith, *J. Physical Chem.*, 1918, **23**, 186) being devoted to the study of occlusion of this gas in the various metals, we may, for purposes of comparison, regard the free energies of the unstable quasi-chemical superficial hydrides or carbonyls as equal or running parallel to their heats of formation and stability, whilst a knowledge of the vapour pressures at different temperatures and the specific heats is required for an exact determination of the free energy at various temperatures.

It will be noted that the ratio H_2/CO burnt increases progressively with the following catalytic materials: iron oxide; iron oxide with promoters; copper oxide; nickel; palladium; this is the order of increase in the stability of the hydrides, the union of palladium and hydrogen being actually exothermic at the ordinary temperature. The rate of evaporation of hydrogen from these surfaces, V_{H_2}, will therefore, under identical conditions, decrease in the above order, or the surface concentration, a_{H_2}, will increase. Hence the ratio a_{CO}/a_{H_2}, which is the ratio of the surface concentrations of the two gases, will alter with the catalytic material, and with this alteration in the surface concentrations there will be a corresponding alteration in the rates of combustion. As the temperature is raised, the rates of evaporation of the gases increase, and thus the specific influence of the catalytic material disappears; this inference is clearly indicated in the curves, where it will be noted that at 400° the ratio is practically independent of the catalyst employed.

Summary.

The selective combustion of carbon monoxide in hydrogen on the surface of catalytic materials is shown to be a case of two simultaneous reactions. The rates of combustion of the two gases between 100° and 400° are related to the composition of the gaseous mixture by the expression:

$$\frac{-\frac{dc_{CO}}{dt}}{-\frac{dc_{H_2}}{dt}} = K\frac{(CO)}{(H_2)(O_2)^{\frac{1}{2}}}.$$

Elevation in temperature causes a decrease in the apparent selective character of the reaction, and the relationship between the influence of temperature and the ratio of gases burnt can be calculated approximately from the conception of the critical increment as developed by Lewis.

The results obtained are in agreement with Langmuir's theory of adsorption, in which the adsorbed layer is considered to be only

one molecule thick; but the surface concentration of each gas is found to be dependent, not only on the nature of the gas, but also of the absorbing surface, indicating that the quasi-chemical combinations between gas and surface possess different free energies and are not simply the result of differences in activation of the reacting gaseous constituents.

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LXXXV.—*The Temperature of Explosion for Endothermic Substances.*

By RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE.

BERTHELOT has shown (*Compt. rend.*, 1887, **105**, 1159; 1899, **129**, 926) that certain endothermic substances which, if heated gradually, would either volatilise or decompose, can be made to explode by throwing them into a vessel previously raised to a suitably high temperature. This result was observed with trinitrophenol, mono-, di-, and tri-nitronaphthalene, and potassium chlorate. The authors, following up these observations of Berthelot, find that for each endothermic substance there is a temperature below which explosive decomposition does not occur, and this definite point is termed the temperature of explosion.

The procedure adopted was to drop a small quantity of the substance to the bottom of a clean test-tube immersed in a bath of potassium hydrogen sulphate just when the temperature of the bath has attained the temperature particular to each substance, as otherwise a simple decomposition would take place. The temperature of this bath, up to 500°, was recorded on a mercury thermometer; at higher temperatures, a thermo-couple was employed. The experiment was carried out in an atmosphere of carbon dioxide, but any other indifferent gas, such as nitrogen, may be used, and explosive decomposition occurs with equal readiness in a vacuum.

From the results recorded below for the temperatures of explosion of various substances, one or two conclusions of a general kind may be drawn. So far as nitro-derivatives are concerned, it appears that, of the disubstituted derivatives of benzene, the ortho-compound, as a rule, has the lowest, and the para-compound the highest, temperature of explosion. Thus the temperatures of explosion for *o*-, *m*-, and *p*-chloronitrobenzene are 614°, 638°, and

720° respectively. In the case, however, of the nitrophenols, the para-compound has a lower temperature of explosion than the meta-compound. For dinitro-compounds with the nitro-group in the meta-position, the temperature of explosion falls as the number of alkyl groups attached to the ring increases. In this connexion, the figures for the temperatures of explosion of *m*-dinitrobenzene, 2:4-dinitrotoluene, and 4:6-dinitro-*o*-xylene may be quoted: they are 580°, 470°, and 438° respectively. The same relation holds good in the case of trinitro-derivatives.

In the following record, the temperature of explosion follows the name of the compound examined.

Nitro-compounds.

o-Dinitrobenzene, 472°; *m*-dinitrobenzene, 580°; 1:3:5-trinitrobenzene, 520°; 2:4-dinitrotoluene, 470°; α-2:4:6-trinitrotoluene, 418°; 4:6-dinitro-*o*-xylene, 438°; 3:4-dinitro-*o*-xylene, 413°; trinitroxylene (m. p. 178°), 408°; 2:4:6-trinitro-*m*-xylene, 410—412°; 2:3:6-trinitro-*p*-xylene, 410°; dinitromesitylene, 418°; trinitromesitylene, 415°; trinitrocumene, 502°; 2:4-dinitrostilbene, 412°; *o*-dinitrostilbene, 420°; α-dinitrodiphenylmethane (m. p. 181°), 335°; 1:6-dinitronaphthalene, 492°; 1:8-dinitronaphthalene, 445°; trinitronaphthalene (m. p. 122°), 364°; tetranitronaphthalene (m. p. 170°), 323°; *o*-chloronitrobenzene, 614°; *m*-chloronitrobenzene, 638°; *p*-chloronitrobenzene, 720°; *p*-bromonitrobenzene, 755°; *p*-iodonitrobenzene, 605°; *o*-nitroaniline, 655°; *m*-nitroaniline, 552°; *p*-nitroaniline, 627°; 2:4-dinitroaniline, 548°; *p*-nitrobenzoic acid, 635°; 2:4-dinitrobenzoic acid, 484°; 3:5-dinitrobenzoic acid, 523°; *o*-nitrophenol, 630°; *m*-nitrophenol, 657°; *p*-nitrophenol, 633°; 2:4-dinitrophenol, 498°; 2:4:6-trinitrophenol, 418°; 3-nitro-*o*-cresol, 503°; 6-nitro-*m*-cresol, 393°; 3:4-dinitro-*o*-cresol, 472°; 3:5-dinitro-*o*-cresol, 455°; 2:4:6-trinitro-*m*-cresol, 405°; 5-nitro-*p*-xylenol, 407°; 3:5-dinitro-*o*-xylenol, 432°; 2:4:6-trinitroresorcinol, 314°; *o*-dinitrodihydroxydiphenyl (m. p. 184°), 447°; 2:6-dichloro-4-nitrophenol, 548°; 4:6-dichloro-2-nitrophenol, 562°; 2:6-dibromo-4-nitrophenol, 625°; 4:6-dibromo-2-nitrophenol, 630°; 2:4:6-tribromo-3-nitrophenol, 605°; 6-bromo-2:4-dinitrophenol, 713°; 2-iodo-3-nitrophenol, 448°; 2:4-di-iodo-6-nitrophenol, 533°; 2:6-di-iodo-4-nitrophenol, 548°.

Picrates.

Ammonium picrate, 423°; hydrazine picrate, 385°; allylamine picrate, 270°; carbamide picrate, 489°; semicarbazide picrate,

474°; guanidine picrate, 498°; hexamethylenetetramine picrate, 360°; aniline picrate, 398°; *o*-toluidine picrate, 400°; α-naphthol picrate, 458°; β-naphthol picrate, 469°; naphthalene picrate, 484°; phenanthrene picrate, 478°; acenaphthene picrate, 418°; pyridine picrate, 432°; quinine picrate, 280°; quinidine picrate, 272°; cinchonine picrate, 268°; cinchonidine picrate, 260°; strychnine picrate, 290°; atropine picrate, 460°.

Azo-compounds.

Azobenzene, 540°; aminoazobenzene, 598°; dimethylaminoazobenzene, 643°; diazoaminobenzene, 703°.

Haloid Compounds.

Iodoform, 295°; *p*-di-iodobenzene, 788°; 2:4:6-tri-iodophenol, 675°; di-iodo-*o*-cresol, 782°; 2:4:6-tri-iodo-*m*-cresol, 696°; 2:4:6-tribromoresorcinol, 713°; 2:4:6-tribromo-orcinol, 793°; pentabromo-orcinol, 698°.

Organic Perchlorates.

Allylamine perchlorate, 262°; methylamine perchlorate, 338°; propylamine perchlorate, 290°; heptylamine perchlorate, 265°; hexylamine perchlorate, 278°; aniline perchlorate, 250°.

o-Toluidine perchlorate.—This salt has not previously been described. It is prepared by neutralising the base with perchloric acid. It does not melt on heating, but slowly carbonises:

0·0993 gave 6 c.c. N_2 at 28° and 760 mm. N = 6·72.

$C_7H_9N,HClO_4$ requires N = 6·76 per cent.

It explodes at 260°.

m-Toluidine perchlorate.—This salt was prepared by the interaction of the hydrochloride of the base and silver perchlorate. It melts and chars at 200°:

0·0804 gave 4·9 c.c. N_2 at 28° and 760 mm. N = 6·78.

$C_7H_9N,HClO_4$ requires N = 6·76 per cent.

It explodes at 300°.

The following perchlorates were prepared by double decomposition, as in the preceding case.

p-Toluidine perchlorate:

0·1027 gave 6·2 c.c. N_2 at 29° and 760 mm. N = 6·70.

$C_7H_9N,HClO_4$ requires N = 6·76 per cent.

It explodes at 278°.

m-4-*Xylidine perchlorate* decomposes at 200°:

0·1000 gave 5·8 c.c. N_2 at 28° and 760 mm. N = 6·45.

$C_8H_{11}N,HClO_4$ requires N = 6·33 per cent.

It explodes at 260°.

p-*Xylidine perchlorate* decomposes at 210°:

0·1072 gave 6 c.c. N_2 at 28° and 760 mm. N = 6·33.

$C_8H_{11}N,HClO_4$ requires N = 6·33 per cent.

It explodes at 258°.

Benzylamine perchlorate melts at 120°:

0·0816 gave 5·2 c.c. N_2 at 28° and 760 mm. N = 7·09.

$C_7H_9N,HClO_4$ requires N = 6·76 per cent.

It explodes at 305°.

Phenylethylamine perchlorate, 280°; α-naphthylamine perchlorate, 228°; menthylamine perchlorate, 308°.

Camphylamine perchlorate melts and decomposes at 215°:

0·0570 gave 3·1 c.c. N_2 at 29° and 760 mm. N = 5·97.

$C_{10}H_{19}N,HClO_4$ requires N = 5·53 per cent.

It explodes at 255°.

Diethylamine perchlorate melts at 107° and is very hygroscopic:

0·1067 gave 7·8 c.c. N_2 at 28° and 760 mm. N = 8·13.

$C_4H_{11}N,HClO_4$ requires N = 8·09 per cent.

It explodes at 282°.

Dipropylamine perchlorate, 308°; diamylamine perchlorate, 323°; benzylethylamine perchlorate, 322°; benzylmethylamine perchlorate, 294°.

Dibenzylamine perchlorate explodes at 290°:

0·0574 gave 2·6 c.c. N_2 at 27° and 760 mm. N = 5·31.

$C_{14}H_{15}N,HClO_4$ requires N = 4·7 per cent.

p-*Tolyltrimethylammonium perchlorate* melts at 192°:

0·0670 gave 3·8 c.c. N_2 at 30° and 760 mm. N = 6·08.

$C_{10}H_{16}N,ClO_4$ requires N = 5·62 per cent.

It explodes at 310°.

Methylpyridinium perchlorate explodes at 362°:

0·0661 gave 4·9 c.c. N_2 at 32° and 760 mm. N = 8·12.

C_6H_9N,ClO_4 requires N = 7·61 per cent.

Ethylpyridinium perchlorate explodes at 340°:

0·0765 gave 4·9 c.c. N_2 at 30° and 760 mm. N = 7·07.

$C_7H_{11}N,ClO_4$ requires N = 6·73 per cent.

Neurine perchlorate, 298°; phenylbenzylmethylammonium perchlorate, 275°; trimethylsulphonium perchlorate, 280°; ethylquinolinium perchlorate, 330°; propylquinolinium perchlorate,

342°; ethylquinaldinium perchlorate, 268°; hydrazine monoperchlorate, 238°; hydrazine diperchlorate, 215°; trimethylenediamine perchlorate, 310°; ethylenediamine perchlorate, 270°.

Guanidine perchlorate melts at 237°:

0·2249 gave 53 c.c. N_2 at 29° and 760 mm. N = 26·15.

$CH_5N_3,HClO_4$ requires N = 26·41 per cent.

It explodes at 367°.

Semicarbazide perchlorate explodes at 278°:

0·0929 gave 20·2 c.c. N_2 at 30° and 760 mm. N = 24·01.

$CH_5ON_3,HClO_4$ requires N = 24·00 per cent.

Piperazine perchlorate melts at 80°:

0·1156 gave 9 c.c. N_2 at 29° and 760 mm. N = 8·64.

$C_4H_{10}N_2,2HClO_4,2H_2O$ requires N = 8·69 per cent.

It explodes at 290°.

o-Phenylenediamine perchlorate explodes at 250°:

0·0310 gave 2·6 c.c. N_2 at 27° and 760 mm. N = 9·31.

$C_6H_8N_2,2HClO_4$ requires N = 9·09 per cent.

m-Phenylenediamine perchlorate, 263°; *p*-phenylenediamine perchlorate, 260°.

Alkaloids, etc.

Brucine, 793°; narcotine, 720°; narceine, 697°; chloralurethane, 673°; oxalylhydrazide, 548°; acetophenoneoxime, 734°; benzil, 643°.

Investigations on similar lines are being continued.

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LXXXVI.—*The Preparation of Butylamine and of* n-*Dibutylamine. The Separation of Aliphatic Amines by Partial Neutralisation.*

By EMIL ALPHONSE WERNER.

THE preparation of *n*-butylamine, and of *n*-dibutylamine, from the interaction of butyl bromide and ammonia in alcoholic solution at the ordinary temperature has been investigated. A procedure similar to that employed in the preparation of the corresponding ethyl derivatives of ammonia was adopted (T., 1918, **113**, 899).

The details of a few experiments on a simple method for the separation of amines from intermediate distillates are recorded, and whilst the results have a practical value as regards the economic preparation of amines on a large scale, they go to show that the prevailing views with respect to the relative basicity of primary, secondary, and tertiary aliphatic amines require to be modified. (Expts. 2, 3, and 4.)

Experimental.

n-Butyl bromide was conveniently prepared by distillation at 98—100° of a mixture of butyl alcohol, sulphuric acid, and sodium bromide in molecular proportions, the temperature being raised to 120° towards the end of the process. The yield of the crude product, dried over calcium chloride, was equal to 92 per cent. of the theoretical, and from 1126 grams there were obtained after redistillation 1082 grams of pure butyl bromide, boiling at 100—101°.

Expt. I.—Four litres of 90 per cent. alcohol were saturated with ammonia until 500 grams of the gas had been dissolved; 200 grams of butyl bromide were added (ratio butyl bromide to NH_3 approximately 1 to 20), after which, at successive intervals of three days, fresh quantities of the alkyl haloid were added as follows: 180, 170, 160, 150, and finally 140 grams. Thus, in all, 1000 grams were added over a period of fifteen days; preliminary tests had shown that nearly all of the butyl bromide was decomposed after three days. Only a few crystals of ammonium bromide separated, and on the twentieth day the alcoholic solution was concentrated by distillation, when 175 grams of ammonium bromide were recovered. As no crystalline matter separated after further concentration, the product was diluted with water and boiled to expel the last traces of alcohol. A dark brown, syrupy liquid (1200 grams) was ultimately obtained, which, analysis showed, contained 399·4 grams of bromine; hence this required 200 grams of sodium hydroxide for the liberation of the total amines present.

Whilst the separation of butylamine (b. p. 76°) from dibutylamine (161°) by distillation was comparatively simple, this was not so as regards the separation of the latter from tributylamine (214°). Hence, in order to avoid tedious fractionations of a mixture of all three amines, fractional treatment with sodium hydroxide was adopted as a preliminary (T., *loc. cit.*).

The product was introduced into a large separating funnel, 40 grams of sodium hydroxide dissolved in 80 c.c. of water were added, and the mixture was vigorously agitated at intervals; after a few hours the layer of 'amine' which had separated was removed.

It weighed 67 grams (dry) and was a mixture of di- and tri-butylamine, in which the latter largely predominated; it was dealt with as described later. (Amine A, Expt. 2.)

After the addition of 80 grams of sodium hydroxide to the residual liquid, followed by brisk agitation, 200 grams of 'amine' (B) were separated. This was distilled, with the aid of a three-bulb pear-shaped still-head, and 109 grams of pure dibutylamine were collected, after 49 grams had passed over between 80° and 158° (dealt with under Expt. 3). The residue, 42 grams, boiling above 161° was added to 'amine' (A). To the remaining solution a final quantity of 80 grams of sodium hydroxide was added, the mixture was transferred to a flask, and the whole of the liberated amine was removed by distillation at 90°. The product, 'amine' (C), weighed 187 grams (dry); it was redistilled, using a three-column evaporator still-head, and 167 grams of pure butylamine (76—77°) were collected. The residue (20 grams) was added to the first distillate (49 grams) from 'amine' (B).

Separation of a Mixture of Dibutylamine and Tributylamine, by Partial Neutralisation with Hydrochloric Acid.

The separation of the mixture of 'amine' (A) with the residue from 'amine' (B) into its constituents by fractional distillation was abandoned as hopeless; thus, for example, whilst the greater part passed over before the boiling point (214°) of tributylamine was reached, the first fraction (162—180°) contained 10·7 per cent. of tributylamine, and the last fraction (200—214°) contained 16·6 per cent. of dibutylamine.

The following simple procedure gave the desired result:

Expt. 2.—The mixture, 98 grams, which on analysis was found to contain 51 grams of dibutylamine, was placed in a separating funnel and 132 c.c. of 3*N*-hydrochloric acid* and 40 c.c. of water were added. The product was thoroughly agitated, and after a few hours the layer of insoluble amine was removed. It weighed 46 grams, and distilled steadily at 212—214°; it was therefore pure tributylamine.

The aqueous solution was evaporated at 100°, and the residue dried over sulphuric acid; it weighed 64·3 grams and contained Cl = 21·46, whilst $(C_4H_9)_2NH,HCl$ requires Cl = 21·45 per cent.

The separation of the two amines was therefore complete.

* The amount of hydrochloric acid required to combine with the dibutylamine only; the extra water was necessary to keep the salt in solution.

Separation of a Mixture of Butylamine and Dibutylamine by Partial Neutralisation with Hydrochloric Acid.

Expt. 3.—The fraction collected between 80° and 158° (49 grams) from the distillation of 'amine' (B) and the residue (20 grams) from the distillation of 'amine' (C) were mixed. Analysis showed that the product contained approximately 48 grams of butylamine. It was well agitated with 220 c.c. of 3*N*-hydrochloric acid in a separating funnel and allowed to remain for twenty-four hours. The solution was extracted twice with 70 c.c. of ether to remove all the free amine. The ethereal solution (previously dried) was distilled, and after removal of the solvent and of a few c.c. of amine which passed over below 161°, 18 grams of pure dibutylamine were collected.

The aqueous solution was evaporated at 100°, and the residue dried over sulphuric acid. It contained Cl = 31·14, whilst $C_4H_9{\cdot}NH_2,HCl$ requires Cl = 32·42 per cent. The weight was 74 grams, and the proportion of butylamine hydrochloride was equal to 86·2 per cent. Whilst the separation in this case was not so complete as in Expt. 2, the results show that on a manufacturing scale the recovery of amines from intermediate distillates and residues could be economically effected by this method.

The total yields of the respective amines were: butylamine, 215 grams = 40·2 per cent.; dibutylamine, 181 grams = 41·1 per cent.; and tributylamine, 47 grams = 10·4 per cent. of the theoretical. When 200 grams of butyl bromide were added to 3 litres of 90 per cent. alcohol, saturated with ammonia as in Expt. 1, and the product worked up after five days, 73 grams of butylamine, equal to 68·5 per cent. of the theoretical, were obtained; the yield of dibutylamine was 28 grams, equal to 31·9 per cent. of the theoretical, and no tributylamine was formed.

The following *n*-butyl derivatives were incidentally prepared in connexion with other work:

Ethyl *n*-butylcarbamate, $C_4H_9{\cdot}NH{\cdot}CO_2Et$, from the interaction of butylamine and ethyl chloroformate dissolved in benzene, was obtained in theoretical yield as a colourless oil which boiled at 202—203°/765·5 mm. (van Erp, *Rec. trav. chim.*, 1895, **14**, 1, gives 100°/15 mm.).

Dibutylcarbamyl chloride, $(C_4H_9)_2N{\cdot}COCl$, a colourless oil, which boiled at 242—243°/755 mm., and became pink on exposure to air, was obtained from the interaction of carbonyl chloride and dibutylamine dissolved in benzene.

Tributylcarbamide, $C_4H_9{\cdot}NH{\cdot}CO{\cdot}N(C_4H_9)_2$, was obtained as a viscous, colourless liquid which boiled at 238—239°/766 mm., by the

action of butylamine on the foregoing compound dissolved in benzene.

as-*Dibutylcarbamide*, $NH_2 \cdot CO \cdot N(C_4H_9)_2$.—The preparation of this derivative furnished an interesting example of the use of benzene in obtaining an anhydrous solid as described by Atkins and Wilson (T., 1915, **107**, 916); and the details are perhaps worth recording. Potassium cyanate was added to an aqueous solution of dibutylamine hydrochloride, and a viscous oil separated rapidly when the solution was heated to 100°. The oil, which was readily soluble in alcohol, ether, chloroform, or benzene, showed no signs of crystallisation * after it had remained for three days in a desiccator over sulphuric acid. The addition of light petroleum to the cold solution in benzene failed to induce crystallisation, and with the object of removing the solvent the mixture was distilled from a flask plunged in hot water. When a portion of the solvent had passed over as a turbid mixture, a sudden copious separation of needle-shaped crystals, melting at 149—150°, took place, while the liquid was still warm.

Found: N = 16·11. $C_9H_{20}ON_2$ requires N = 16·28 per cent.

The compound is very hygroscopic; it liquefies after exposure to the air for a few minutes.

Separation of Diethylamine from Triethylamine by Partial Neutralisation with Hydrochloric Acid.

The following experiment supplies a further illustration of the use of this method.

Expt. 4.—In the preparation of a considerable quantity of diethylamine, a fraction was collected between 75° and 91°; it had the composition $NHEt_2$ = 6·74 per cent., NEt_3 = 93·26 per cent. It weighed 146 grams, and therefore contained 9·84 grams of diethylamine. It was mixed with 67 c.c. of 2*N*-hydrochloric acid and treated as described in Expt. 3.

The free amine was collected without loss and boiled at 90—91°, the boiling point of pure triethylamine.

The hydrochloride recovered from the aqueous solution contained Cl = 32·22, whilst $(C_2H_5)_2NH,HCl$ requires Cl = 32·42 per cent.

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* Monobutylcarbamide melts at 86°; disubstituted carbamides of the above type generally melt at a much higher temperature than the monosubstituted derivatives.

LXXXVII.—*The Abnormal Behaviour of Glyoxalinecarboxylic Esters and Anilides towards Diazonium Salts.*

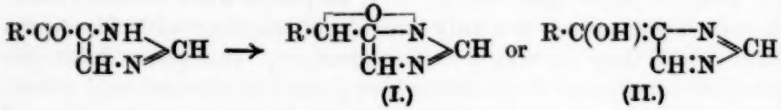
By Robert George Fargher and Frank Lee Pyman.

In a recent paper (this vol., p. 217), we put forward evidence showing that glyoxalines are only capable of coupling with diazonium salts when they contain a free imino-group and also a hydrogen atom or some other displaceable group, such as the carboxyl group, in one of the 2-, 4-, or 5-positions. Numerous derivatives of glyoxaline, in which these conditions are fulfilled, have been shown to couple with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, but an exceptional behaviour is shown by the esters of 5-methylglyoxaline-4-carboxylic acid (Gerngross, *Ber.*, 1912, **45**, 513) and the esters of glyoxaline-4-carboxylic acid (Pyman, T., 1916, **109**, 186). These give a negative result, whereas the corresponding acids behave normally, giving deep red solutions with the reagent.

With the object of finding some clue to this abnormality, we have examined the behaviour of a number of carboxylic acids containing the glyoxaline nucleus and their esters towards sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. All the acids examined gave a positive result, and so also did the esters of those acids, such as glyoxalineacetic acid, in which the carbonyl group is separated from the glyoxaline nucleus by a chain of one or more carbon atoms. The esters of the 2-alkylglyoxaline-4-carboxylic acids, however, like those of glyoxaline-4-carboxylic acid and 5-methylglyoxaline-4-carboxylic acid, gave a negative result, and so also did the anilides of glyoxaline-4-carboxylic acid and its 2-alkyl derivatives. In order to ensure that the difference in behaviour was not due to the particular conditions selected for the test, the action of benzenediazonium chloride and *p*-nitrobenzenediazonium chloride on glyoxaline-4-carboxylic acid and ethyl glyoxaline-4-carboxylate was examined. In the presence of hydrochloric acid or acetic acid, neither of the derivatives coupled, whilst in the presence of sodium carbonate or sodium hydroxide the acid coupled but the ester did not.

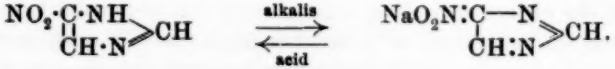
The abnormality is thus seen to be connected with the direct attachment of the carboxyalkyl or carboxyanilide group to the glyoxaline nucleus, and would seem to be due to the mutual influence of the imino- and carbonyl groups.

Further than this we do not as yet feel able to offer any explanation of the abnormality. The fact that all the glyoxalinecarboxylic esters and anilides behave normally towards silver nitrate in ammoniacal solution, yielding insoluble silver salts, rules out any formula such as (I) not containing a free iminic or acidic hydrogen atom, whilst their stability towards potassium permanganate in acid solution would appear to indicate that they exist as true glyoxalines in the presence of mineral acids.



(I.) (II.)

There is, however, the possibility of a molecular rearrangement, such as that represented by formula (II), taking place under the influence of alkalis. The nitroglyoxalines also fail to couple with diazonium salts, and here the explanation seems clear, since these compounds dissolve in alkalis with a yellow colour, yielding salts which are no doubt derived from the corresponding nitronic acids, as Windaus (*Ber.*, 1909, **44**, 758) has suggested, and no longer contain an imino-group.



The glyoxalinecarboxylic esters and anilides, however, yield colourless solutions with alkalis, and although, bearing in mind that the nitroglyoxalines themselves are colourless and their alkaline solutions only comparatively pale yellow, the lack of colour would alone seem insufficient to preclude a formula such as (II), we do not feel justified in advancing it as more than a possibility until further experimental evidence has been accumulated.

While seeking for comparable instances of the mutual influence of imino- and carbonyl groups, we have observed that whereas anthranilic acid couples with sodium diazobenzene-*p*-sulphonate or *p*-nitrobenzenediazonium chloride in sodium carbonate solution, ethyl anthranilate gives a negative result. Both, of course, couple in acid solution. Further, it is perhaps worth noting that whereas the hydrochloride of anthranilic acid is stable in aqueous solution, the hydrochlorides of its methyl and ethyl esters are readily hydrolysed in cold aqueous solution with liberation of the free ester (compare Kolbe, *J. pr. Chem.*, 1884, [ii], **30**, 474; Fränkel and Spiro, *Ber.*, 1895, **28**, 1686; E. and H. Erdmann, *Ber.*, 1899, **32**, 1213), and whilst *s*-ethylenebisanthranilic acid dissolves readily in dilute

mineral acids, the corresponding methyl ester is insoluble even in excess (Fränkel and Spiro, *loc. cit.*).

Experimental.

The esters described in this communication were prepared by boiling the acids with absolute alcohol saturated with hydrogen chloride. After removing the excess of alcohol and adding cold saturated aqueous potassium carbonate, the esters of the 2-alkylglyoxaline-4-carboxylic acids separated in a crystalline state. The other esters were extracted from the solutions by means of chloroform, and crystallised either as base or as hydrogen oxalate.

Ethyl 2-methylglyoxaline-4-carboxylate crystallises from ethyl acetate in clusters of fine, shimmering needles, which melt at 156° (corr.) and are anhydrous. It is sparingly soluble in water, but readily so in alcohol or ethyl acetate.

Found: C = 54·3; H = 6·7; N = 17·9.

$C_7H_{10}O_2N_2$ (154·1) requires C = 54·5; H = 6·5; N = 18·2 per cent.

The ester gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

2-Ethylglyoxaline-4-carboxylic Acid and its Derivatives.

2-Ethylglyoxaline-4-carboxyanilide is prepared from 2-ethylglyoxaline-4:5-dicarboxylic acid in a yield amounting to 45 per cent. of the theoretical by the general method described in a previous communication (this vol., p. 217). It is readily soluble in alcohol but very sparingly so even in boiling water, from which it crystallises in clusters of fine needles; these are anhydrous and melt at 193° (corr.), sintering from 190°. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found: C = 66·6; H = 5·8; N = 19·2.

$C_{12}H_{13}ON_3$ (215·2) requires C = 66·9; H = 5·6; N = 19·5 per cent.

2-Ethylglyoxaline-4-carboxylic acid is obtained in good yield by the hydrolysis of the corresponding anilide by dilute hydrochloric acid at 130°. It is readily soluble in hot water, but sparingly so in cold, and crystallises from the former in well-defined, prismatic needles which contain two molecules of water of crystallisation. After drying at 110°, it melts at 252° (corr.), sintering from 248°. It gives an immediate blood-red coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found, in air-dried acid: loss at 110° = 20·7.

$C_6H_8O_2N_2,2H_2O$ requires 20·5 per cent.

In acid dried at 110°, C=51·3; H=5·7; N=19·9.

$C_6H_8O_2N_2$ (140·1) requires C=51·4; H=5·8; N=20·0 per cent.

The *picrate* crystallises from water in large, prismatic needles containing one and a-half molecules of water of crystallisation. After drying at 60° in a vacuum, it sinters above 170° and forms a turbid liquid, which becomes clear at about 195°.

Found, in air-dried salt, H_2O=6·9.

$C_6H_8O_2N_2,C_6H_3O_7N_3,1\frac{1}{2}H_2O$ requires 6·8 per cent.

In dried salt, N=18·7.

$C_6H_8O_2N_2,C_6H_3O_7N_3$ (369·2) requires N=19·0 per cent.

Ethyl 2-ethylglyoxaline-4-carboxylate crystallises from ethyl acetate, in which it is readily soluble, in prismatic needles which melt at 129° (corr.), and are anhydrous. It is readily soluble in alcohol, but sparingly so in water. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found: C=56·8; H=7·2; N=16·5.

$C_8H_{12}O_2N_2$ (168·2) requires C=57·1; H=7·2; N=16·6 per cent.

2-Phenylglyoxaline-4-carboxylic Acid and its Derivatives.

2-Phenylglyoxaline-4-carboxyanilide is prepared by the action of boiling aniline on 2-phenylglyoxaline-4:5-dicarboxylic acid in a yield amounting to 74 per cent. of the theoretical. As it is practically insoluble in boiling water, it is left behind after the steam distillation somewhat contaminated by resinous impurities, which are readily removed by grinding and washing with ice-cold alcohol. It is sparingly soluble in alcohol or the other usual organic solvents, and separates from alcohol in minute, glistening needles, which melt at 263° (corr.) and are anhydrous. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found: C=72·6; H=5·3; N=15·9.

$C_{16}H_{13}ON_3$ (263·2) requires C=73·0; H=5·0; N=16·0 per cent.

2-Phenylglyoxaline-4-carboxylic acid is obtained in good yield by the hydrolysis of the corresponding anilide, which, however, is much more stable towards acid hydrolysis than the 2-alkyl derivatives. At 130° the reaction proceeds very slowly, but at 145—150° the reaction is complete after eight to nine hours' heating. The acid separates from boiling water, in which it is fairly readily soluble, in fan-shaped clusters of minute needles containing one and a-half molecules of water of crystallisation. After drying at 110°, it melts and effervesces at 239° (corr.). The acid gives an immediate

red coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found, in air-dried material: loss at 110° = 12·7.

$1\frac{1}{2}H_2O$ requires 12·6 per cent.

In substance dried at 110°, C = 63·5; H = 4·5; N = 14·8.

$C_{10}H_8O_2N_2$ (188·1) requires C = 63·8; H = 4·3; N = 14·9 per cent.

Ethyl 2-phenylglyoxaline-4-carboxylate crystallises from ethyl acetate in minute needles, which melt at 189° (corr.), sintering above 183°. It is readily soluble in alcohol or hot ethyl acetate, less readily so in cold ethyl acetate, and very sparingly so in water. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found, in air-dried substance: loss at 100° = 9·5.

Found, in dried substance: C = 66·5; H = 5·7; N = 12·9.

$C_{12}H_{12}O_2N_2$ (216·1) requires C = 66·6; H = 5·6; N = 13·0 per cent.

Ethyl Glyoxaline-4-acetate.—This was prepared previously by the action of alcoholic hydrogen chloride on 4-cyanomethylglyoxaline (T., 1911, **99**, 681), and can also be obtained by the esterification of the corresponding acid or by the action of alcohol on the hydrochloride of glyoxaline-4-acetyl chloride. It gives a deep red colour when mixed with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

Glyoxaline-4-acetyl chloride hydrochloride can be prepared in a crystalline state by the method given below. The crude product contains less than the theoretical amount of chlorine, and we have been unable to devise a satisfactory method of purifying it.

Five grams of phosphorous pentachloride and 6 c.c. of thionyl chloride were heated on the water-bath to incipient ebullition (about 50°), and 4 grams of glyoxaline-4-acetic acid hydrochloride were added, the mixture being well stirred. Evolution of hydrogen chloride took place, and the pasty mass quickly became crystalline, forming minute leaflets. When the reaction had ended, the mass was diluted with chloroform, filtered, washed with chloroform, and dried in a vacuum over sulphuric acid and sodium hydroxide. The dry, crystalline powder obtained in this way was pale pink and amounted to 4·4 grams, that is, 97·7 per cent. of the theoretical. The specimen with the highest chlorine content melted and decomposed at 127° (corr.), the others at 125°.

Found: C = 33·2; H = 3·5; Cl = 35·5, 35·1, 36·8 (in different specimens).

$C_5H_5ON_2Cl,HCl$ (181·0) requires C = 33·2; H = 3·3; Cl = 39·2 per cent.

Ethyl β-Glyoxaline-4-propionate.—This was purified by crystallisation of the hydrogen oxalate from alcohol. The ester formed an oil, which gave an immediate blood-red colour with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

The *hydrogen oxalate* separates from alcohol in colourless, shimmering leaflets, which are anhydrous and melt at 160° (corr.) after sintering from 155°. It is readily soluble in water or hot alcohol, but sparingly so in cold alcohol.

Found: C = 48·1; H = 6·0; N = 11·8.

$(C_8H_{12}O_2N_2)_4(C_2H_2O_4)_3$ (942·7) requires C = 48·4; H = 5·8; N = 11·9 per cent.

Ethyl α-hydroxy-β-glyoxaline-4-propionate crystallises from dry chloroform in minute, colourless plates which melt at 118—119° (corr.), and are anhydrous. It is readily soluble in water or alcohol, sparingly so in chloroform, and insoluble in ether. It gives a cherry-red colour with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

Found: C = 52·3; H = 6·5.

$C_8H_{12}O_3N_2$ (184·1) requires C = 52·2; H = 6·6 per cent.

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LONDON, E.C. 1. [*Received, July 12th*, 1919.]

LXXXVIII.—*The Free Energy of Dilution of Aqueous Sodium Chloride Solutions.*

By ARTHUR JOHN ALLMAND and WILFRID GUSTAV POLACK.

THIS work, which was commenced a few months prior to the outbreak of war, was undertaken with the view of investigating systematically the relations existing between activity and concentration for the different molecular species present in aqueous solutions of typical binary electrolytes, working between the limits of saturated solutions and solutions of dilution only determined by difficulties of measurement. G. N. Lewis, to whom we owe the introduction into thermodynamics of the term "activity" (*Zeitsch. physikal. Chem.*, 1907, **61**, 129), has also provided a very convenient way of expressing the deviations—true or apparent—from the laws of perfect solutions which are exhibited by the ions and by the molecules of undissociated electrolyte, namely, by the use of the magnitude "activity coefficient." The "activity coefficient" of a

chemical species in any phase is the ratio activity/concentration for that species in the given phase. In the case of electrolytes, activity can be measured by any of the related thermodynamic methods (that is, osmotic pressure, lowering of freezing point, electromotive force), whilst the concentration can be determined from conductivity methods, with or without the rather uncertain correction for viscosity. The extent to which the activity coefficient differs from unity and changes in magnitude with change of concentration is a measure of the abnormality of the thermodynamic behaviour of the chemical species in question under the experimental conditions.

The same author (*J. Amer. Chem. Soc.*, 1912, **34**, 1631), in an important critical survey of the subject, discusses the then available experimental data, including measurements of solubility product, depression of freezing point, and electromotive force. Assuming the validity of the conductivity method of arriving at concentration values, the conclusion drawn is that, whilst in very dilute solutions concentrations and activities of ions are directly proportional, their activity coefficients fall off somewhat as the solutions become more concentrated. On the other hand, the activity coefficients of the undissociated molecules of electrolytes increase rapidly with increase of concentration. Specific effects for ions would appear to enter at concentrations higher than 0·1*N*. Later in his paper, he seriously disputes the basis of the Kohlrausch method of arriving at the ionic and undissociated-molecule concentrations, believing it to be vitiated by changes in the mobility of ions with concentration, a view first put forward by Jahn (*Zeitsch. physikal. Chem.*, 1900, **33**, 545). His final conclusion is that ionic activities and concentrations are proportional in dilute solutions up to 0·1*N*, the activity coefficients therefore being unity throughout this region.

These views have been much discussed during the last few years. The conclusion generally drawn (see, for example, Bates, *J. Amer. Chem. Soc.*, 1915, **37**, 1421) is that the conductance–viscosity ratio is a measure of concentration, leaving unexplained the undoubted discrepancies between activity and concentration even in dilute solutions. When the present measurements were undertaken, however, the matter had still to be regarded as an open one. One point which it was hoped to elucidate was the magnitude of the specific effects, if any, in the variations of the activity coefficients of the ions with concentration. By making measurements with four different electrolytes, such as MA, MB, NA, and NB, and by comparing these with one another at concentrations at which the ionic concentrations in the solutions of the four different electro-

lytes, as determined by the conductance–viscosity ratio, are identical, it should be possible to test this point for the ions M', N', A', and B'. Hitherto, the assumption—a probable one—has been made that the activities of the two ions are identical in any solution of a binary electrolyte where their concentrations, excluding complex-formation and solvation, are necessarily the same.

The electromotive force method of measurement was chosen. Tolman and Ferguson* (*J. Amer. Chem. Soc.*, 1912, **34**, 232) had already used it successfully for measurements of activity coefficient on dilute aqueous solutions of hydrochloric acid. It was intended to use as electrolytes the chlorides, bromides, iodides, hydroxides, and sulphates of sodium, potassium, and lithium, and one of the authors had already found (T., 1914, **105**, 1941) the amalgam electrodes prepared according to the directions of G. N. Lewis and his co-workers (*J. Amer. Chem. Soc.*, 1910, **32**, 1459; 1912, **34**, 119) to function satisfactorily.

The principle of the method is briefly as follows. If two cells are set up,

(1) Electrode reversible to ion *A*.	Solution of AB. Concentration C_1.	Electrode reversible to ion *B*.
(2) Electrode reversible to ion *A*.	Solution of AB. Concentration C_2.	Electrode reversible to ion *B*.

the electrode systems being identical, and the two combinations only differing in the values of the concentrations C_1 and C_2 ($C_1 > C_2$), the difference between the electromotive forces of the two cells (E) is a measure of the free energy of dilution of AB from the concentration C_1 to the concentration C_2. If the ions are both univalent, the free energy of dilution per gram-molecule is expressed by

$$FE = RT \ln \frac{[a_1]_{\text{undiss.}}}{[a_2]_{\text{undiss.}}} = RT \ln \frac{[a_1]_A \cdot [a_1]_B}{[a_2]_A \cdot [a_2]_B},$$

where a represents activity and the suffixes refer to the two solutions and to the undissociated molecules and the different ions. Making the assumption mentioned above that $[a]_A = [a]_B$ for the same solution, we have

$$FE = 2RT \ln \frac{[a_1]_{\text{ion}}}{[a_2]_{\text{ion}}}.$$

The measurements of electromotive force allow, therefore, the immediate calculation of activity ratios for the solutions concerned, and from these, using concentration data obtained from measure-

* Professor G. N. Lewis informed us by letter that Professor Tolman had no intention of continuing the work further.

ments of conductivity, the activity coefficient ratios follow immediately.

In order to calculate heats of dilution, measurements were carried out at 18° and 25°. Their close proximity was compensated for by the possibility of utilising the existing conductivity data for calculations of concentration.

Measurements with sodium chloride were completed before the end of 1914. It has been impossible to resume the work, and the results are consequently published as they stand.

Several papers dealing with the same or with closely related problems have been published in America in the interval. Such are those of Bates (*loc. cit.*), MacInnes and Parker (*J. Amer. Chem. Soc.*, 1915, **37**, 1445), Forbes and Anderegg (*ibid.*, 1676), Harned (*ibid.*, 2460; 1916, **38**, 1986; 1918, **40**, 1461), Ellis (*ibid.*, 1916, **38**, 787), Ferguson (*J. Physical Chem.*, 1916, **20**, 326), Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 615, 2601), Noyes and Ellis (*ibid.*, 2532), Pearce and Mortimer (*ibid.*, 1918, **40**, 509), and Rodebush (*ibid.*, 1204). Some of these will be referred to later.

Experimental.

The sodium amalgam was prepared precisely as described by Lewis and Kraus (*loc. cit.*), except that the mercury was distilled over more rapidly on to the sodium by enclosing the containing vessel in an asbestos oven, the mercury being heated to about 280° and the sodium to 130°. The mercury employed, both for making the amalgams, as also for the calomel electrodes, was purified by passing at least twice down the usual column of acid mercurous nitrate. The amalgam was indistinguishable from mercury in appearance, and remained so for more than four years.

The amalgam electrode vessels were as designed by Lewis and Kraus. The calomel electrode vessels used were chiefly (see, however, later) of the usual Ostwald type, the connecting tubes being made as short and as wide as practicable in order to diminish the resistance. The calomel, after being washed several times by shaking with a small quantity of the solution and a little mercury, was shaken with a larger quantity of the solution, the liquid with the calomel in suspension being drawn into the carefully cleaned and dried electrode vessels. From four to six electrodes were prepared for each concentration of sodium chloride solution for which the electromotive force was measured, and, after allowing time for their potentials to become constant (usually eighteen hours), they were compared against one another. Electrodes which agreed at 18° were always found to agree at 25°. When several electrodes

had been obtained showing a maximum difference between any pair of about 0·3 millivolt, one of them was chosen for the actual measurements (or one for the measurements at 18° and another for 25°), and generally compared again with the others after the measurements.

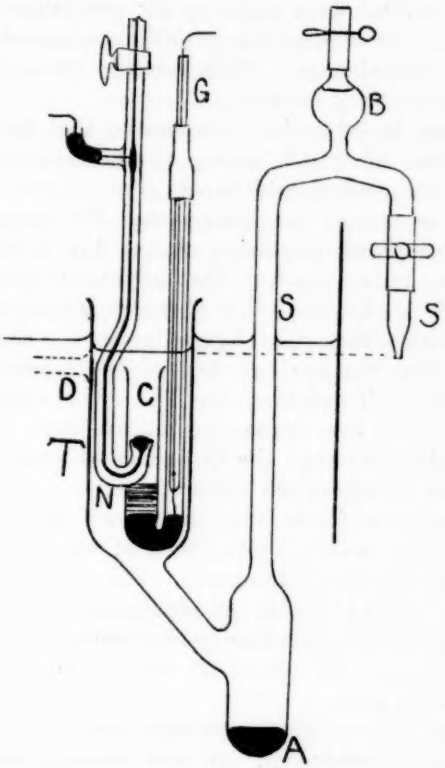
In all, seven concentrations of sodium chloride were employed, namely, 5·41*N* (saturated at 18°),* 3*N*, *N*, 0·5*N*, 0·1*N*, 0·02*N*, and 0·01*N*. The solutions were made up to volume at 18°. With solutions of concentration 0·5*N* and above, the measurements can readily be carried out with considerable accuracy. The solution is contained in a glass tube 10 cm. long and 3·5 cm. in diameter, suitably clamped in the thermostat, and into this tube dip the nozzles of the amalgam and calomel electrodes, also clamped to separate stands. The essential parts of the calomel electrode are also in the thermostat. While the measurement is being made, amalgam drops very slowly from the nozzle of the electrode, and the electromotive force remains practically constant.

With the more dilute solutions, however, several difficulties arise. The most serious of them is the decomposition of the amalgam on coming into contact with the solution. As pointed out by Lewis and Kraus, the decomposition takes place chiefly on small specks floating on the surface of the amalgam, and when the electrode has been in use for a minute or so, these are carried away. Nevertheless, the amalgam which collects at the foot of the tube containing the solution continues to decompose, and there is always some visible decomposition at the nozzle of the electrode, even when the surface seems to be perfectly clean. This tends to make the potential of the electrode less negative in two ways, namely, (i) by increasing the sodion concentration in the liquid surrounding the nozzle of the electrode, and (ii) by decreasing the sodium concentration in the surface layers of the amalgam. The effect of (i) obviously increases rapidly with increasing dilution, not only because of the increase in the actual rate of decomposition, but also because of the relatively larger effect produced on the concentration of the sodions. The consequence of (ii) is that the potential fluctuates, rising suddenly as each drop of amalgam becomes detached, exposing a fresh surface. To counteract this, it is necessary to allow the amalgam to flow more rapidly from the electrode, and this means still more decomposition in the liquid. In consequence of these facts, it was found necessary for the measurements with dilute solutions to use an apparatus of the type shown in Fig. 1, in which the product of decomposition is

* This solution was actually made up to saturation, and its concentration calculated from the available data, not experimentally determined.

prevented from accumulating round the electrode. In its first form, solution flowed from a large dropping funnel into the tube *T*, and up through the siphon tube *S*. The amalgam dropping from the electrode *N* collected at *A*, the alkali formed by the decomposition being thus carried away from the electrode, which was always surrounded by fresh solution. Hydrogen produced at *A* collected at *B*. *C* is the calomel electrode described below.

FIG. 1.



Later, the apparatus was modified so that the solution did not flow directly into the tube *T*, but passed first through a close-wound spiral of thin-walled tubing immersed in the thermostat and sealed into the tube *T* at *D*. With the 0·01*N*-solution, the flow of electrolyte at the moment of measurement must be fairly rapid, and this precaution becomes essential to ensure that the temperature of the solution is accurately that of the thermostat.

Another difficulty which arises with the more dilute solutions is

the comparatively high resistance of the ordinary type of calomel electrode. For the 0·01*N*-measurements, the form shown in Fig. 1 was employed. *C* is the electrode vessel proper, contact being made with the mercury by means of a platinum wire sealed into the end of a narrow glass tube, *G*. When the electrode was not actually in use, the mouth of the tube *C* was closed by a cork, a little of the liquid being removed by a pipette, care being taken not to disturb the calomel at the foot of the tube. These electrodes had a much lower resistance than the others, but were less trustworthy. Several were made up for preliminary tests, and in one or two instances considerable variations occurred, probably due to mechanical disturbances. With suitable precautions, however, they proved satisfactory enough.

In the present investigation, it appeared that the limit of dilution was reached at 0·01*N*, owing to the decomposition of the amalgam. Much greater disturbances occurred between individual readings than in any of the other cases. The electromotive force tended to increase with increasing rate of flow of the electrolyte,* even until the latter reached the maximum possible with the apparatus used, so that the effect of decomposition was apparently never quite eliminated. The figures given for this dilution are therefore less trustworthy than any of the others. One would expect these to be, if anything, too low. The values obtained by extrapolation would also appear to indicate this. They are probably more trustworthy than the experimental values, and are used instead of these in subsequent calculations.

The electromotive forces were measured with a Clark-Fisher potentiometer and cadmium cell, both of which had been tested at the National Physical Laboratory. The potentiometer could be read to 0·0001 volt as long as the resistance in the circuit was not excessively high. Potentiometer, galvanometer, cells, etc., and also the stands to which the electrodes were clamped, were all carefully insulated on glass.

In all, three different amalgams were prepared, each being contained in a pair of electrodes. In each measurement several readings were taken with each electrode with various rates of flow of the amalgam, and, where the special apparatus was used (0·1*N* and more dilute solutions), with various rates of flow of electrolyte. The difference between the values obtained for the two electrodes was in every case less than the possible experimental errors due to other sources. The figures given represent in each

* Incidentally this shows that the flowing electrolyte had reached the temperature of the bath, as the electromotive force increases with rise of temperature.

case the mean of the various individual readings with the two electrodes (in some cases of two or more complete sets of such readings), together with the maximum error likely to be involved, taking into account the variations in the individual readings in the calomel electrodes themselves, etc.

The three pairs of electrodes contained amalgams with the following respective percentages of sodium:

(*a*) 0·2234; (*b*) 0·1657; (*c*) 0·1389.

These values were determined by weighing out small quantities of the amalgam, acidifying, and, on completion of the decomposition, estimating the excess of acid by titration.

The electrodes (*a*) contained only a small quantity of amalgam, and were only used for two dilutions, namely, 0·1*N* and 0·02*N*. As the measurements were carried out with stationary electrolyte and not with the special apparatus, there was a fair amount of decomposition. The values must therefore be regarded as more or less preliminary. Nevertheless, there is good agreement between the values for the difference of electromotive force at 0·1*N* and 0·02*N* furnished by the two pairs of electrodes (*a*) and (*b*), the special apparatus being used in the case of (*b*).

Tables I and II give the actually measured electromotive forces in volts at 18° and 25° for the three amalgams (*a*), (*b*), and (*c*).

TABLE I.

18°.

Concentration.	(*a*)	(*b*)	(*c*)
5·41*N*	—	—	2·0281±0·0002
3*N*	—	—	2·0770±0·0001
1*N*	—	2·1466±0·0002	2·1398±0·0002
0·5*N*	—	2·1792±0·0003	—
0·1*N*	2·2635±0·0010	2·2534±0·0004	—
0·02*N*	2·3384±0·0010	2·3274±0·0005	—
0·01*N*	—	—	2·350 ±0·002

TABLE II.

25°.

Concentration.	(*a*)	(*b*)	(*c*)
5·41*N*	—	—	2·0283±0·0001
3*N*	—	—	2·0784±0·0001
1*N*	—	2·1499±0·0002	2·1430±0·0002
0·5*N*	—	2·1838±0·0003	—
0·1*N*	2·2710±0·0010	2·2596±0·0003	—
0·02*N*	2·3450±0·0010	2·3336±0·0010	—
0·01*N*	—	—	2·358 ±0·002

Assuming that the difference in potential between amalgams (*b*) and (*c*) as deduced from the readings with *N*-solutions is 0·0068

volt at 18° and 0·0069 volt at 25°, the values which the electromotive forces would have for amalgam (*c*) and 0·5*N*-, 0·1*N*-, and 0·02*N*-solutions can be calculated. They are contained in table III and are plotted in Fig. 2. In view of what has already been said (see p. 1026), the figures for 0·01*N*-solutions given in the table are not the experimental values, but those extrapolated from the curve.

FIG. 2.

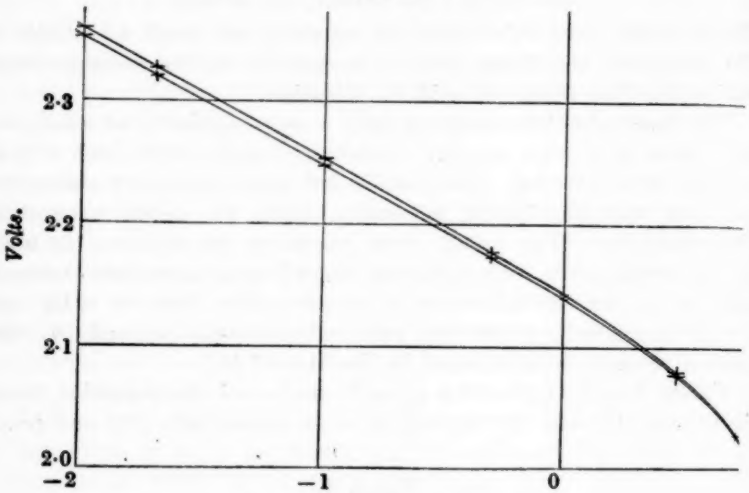


TABLE III.

C in mols. NaCl per litre.	*C* in mols. NaCl per 1000 grams of water.	*E.M.F.* for the combination Hg | Hg_2Cl_2 aqueous NaCl | 0·1389 per cent. sodium amalgam. 18°. Volts.	25°. Volts.	α (defined by $e_t = e_{18}[1+(t-18)\alpha]$).
5·41	6·12	2·0281	2·0283	141×10^{-7}
3·0	3·196	2·0770	2·0784	963
1·0	1·022	2·1398	2·1430	2140
0·5	0·5034	2·1724	2·1769	2960
0·1	0·1003	2·2466	2·2527	3880
0·02	0·02003	2·3206	2·3267	3760
0·01	0·01001	2·3520	2·3585	3950
		(±0·0005)	(±0·0005)	

Free and Total Energy Changes of Cell Reaction.

Taking the Faraday as 96,540 coulombs, the decreases in free and total energy of the system per gram-equivalent transformed can be calculated for the cell reaction

$2Na$ (in form of 0·1389 per cent. amalgam) $+ Hg_2Cl_2 \longrightarrow 2Hg + 2NaCl$ (in aqueous solution)

from the figures in table III. The results are contained in table IV.

TABLE IV.

C in mols. NaCl per 1000 grams of water.	Free energy decrease at 18°. Joules.	Free energy decrease at 25°. Joules.	Total energy decrease at 18°. Joules.
6·12	195795	195815	195000
3·196	200520	200650	195030
1·022	206575	206885	193690
0·5034	209725	210160	191600
0·1003	216885	217475	192360
0·02003	224030	224620	199500
0·01001	227060	227695	200790

The figures indicate that the decrease of total energy, or heat effect of the reaction, at first falls off as the electrolyte becomes more dilute, and then commences to increase. The results are plotted in Fig. 3, and it will be seen that the curve has a minimum at about 0·25—0·3 molecule of sodium chloride per 1000 grams of water. Too much stress, however, is not laid on this result, or on certain other calculations of heat effects recorded subsequently in this paper. The range of temperature over which measurements were made is small, and the calculations are correspondingly affected, whilst for the more dilute solutions the possible errors in the measurements must be seriously taken into account.

Sodium Chloride Concentration Cells without Transference.

By subtracting the values of electromotive force given in table III from the corresponding values for the 0·1N-solution, figures are obtained for the electromotive forces of sodium chloride concentration cells "without transference," one of the two solutions in every case being 0·1N (p. 1022). These values are contained in table V.

TABLE V.

C in mols. NaCl per 1000 grams of water.		$E.M.F.$ at 18°. Volts.	$E.M.F.$ at 25°. Volts.	α (defined by $e_t = e_{18}[1+(t-18)\alpha]$).
C_1.	C_2.			
6·12	0·1003	0·2185	0·2244	386×10^{-5}
3·196	,,	0·1696	0·1743	396
1·022	,,	0·1068	0·1097	388
0·5034	,,	0·0742	0·0758	308
0·02003	,,	−0·0740	−0·0740	0
0·01001	,,	−0·1054	−0·1058	54

We can compare these figures with those obtained by other investigators for similar cells. Thus, whilst for $\frac{C_1}{C_0} = \frac{0{\cdot}1}{0{\cdot}01}$ (normal concentrations) sodium chloride gives a figure of 0·1058 volt at 25°, other experimenters have obtained the following figures for hydrochloric acid and for potassium and lithium chlorides:

FIG. 3.

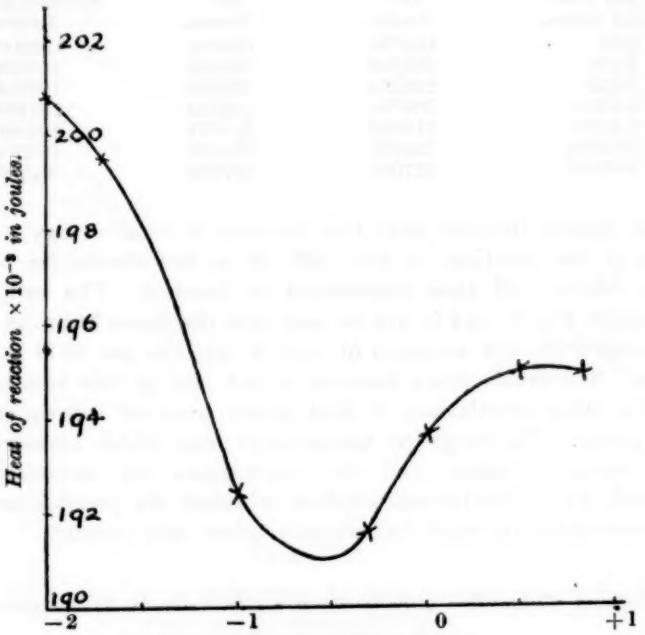


TABLE VI.

Electrolyte.	Volt.	Observer.
HCl	0·114	Noyes and Ellis (*loc. cit.*)
KCl	0·1089	MacInnes and Parker (*loc. cit.*)
LiCl	0·10433	Pearce and Mortimer (*loc. cit.*)

By a comparison of the figures for such cells with those given by the corresponding cells with transference, the transport number of the electrolyte can be calculated. The electromotive force of the cell without transference (p. 1022) is $e_1 = 2\frac{RT}{F} ln \frac{a_1}{a_2}$, whilst that of the cell with transference is $e_2 = 2N\frac{RT}{F} ln \frac{a_1}{a_2}$, where N is the

cation transport number if electrodes reversible to the anion are employed. Consequently,

$$N_c = \frac{e_2}{e_1}$$

Measurements of sodium chloride concentration cells with transference were carried out at 18° by Jahn (*Zeitsch. physikal. Chem.*, 1902, **41**, 298), using calomel electrodes and dilute solutions of electrolyte. Table VII contains figures taken from his paper, together with corresponding values drawn from table V or Fig. 2. In the last column are the calculated transport numbers for the sodium ion.

TABLE VII.

C_1 in mols. per litre.	C_2 in mols. per litre.	e_1.	e_2.	N_c.
0·02	0·01	0·0314	0·01293	0·412
0·04	0·02	0·0317	0·01268	0·400
0·06	0·03	0·0318	0·01255	0·394

Experimental determinations gave the following results (Abegg, "Handbuch," II, i, 231):

C.	$t°$.	N_c.	Observer.
3—5N.	10°	0·352	Hittorf.
0·7N.	16	0·366	,,
0·005N.	10	0·379	,,
1/30—1/150N.	0	0·387	Jahn-Schulz.
1/8—1/14N.	18	0·395	,,
1/8—1/150N.	30	0·404	,,

In a way exactly similar to that by which the figures in table V were obtained from the data of table III, we can calculate from table IV values for the decrease in total energy (heat content) and free energy associated with the transfer of one molecule of sodium chloride from any concentration given in the table to a 0·1 molar normal solution. Table VIII contains the results.

TABLE VIII.

C in mols. NaCl per 1000 grams of water.		Free energy decrease in joules at		Total energy decrease in joules at 18°.
C_1.	C_0.	18°.	25°.	
6·12	0·1003	21090	21660	−2640
3·196	,,	16365	16825	−2670
1·022	,,	10310	10590	−1330
0·5034	,,	7160	7315	+760
0·02003	,,	−7145	−7145	−7145
0·01001	,,	−10175	−10220	−8430

In table IX, the results in the last column of table VIII are expressed as the total energy decrease attending the transfer of

one molecule of sodium chloride from a concentration of 6·12 molecules per 1000 grams of water to other concentrations given in the first column.

TABLE IX.

C in mols. NaCl per 1000 grams of water.	Heat effect at 18°. Joules.	Calories.
6·12	—	—
3·196	+30	+7
1·022	−1310	−313
0·5034	−3400	−812
0·1003	−2640	−630
0·02003	+4505	+1075
0·01001	+5790	+1382

The curve representing the variation of the heat effects of tables VIII and IX with concentration of electrolyte will, of course, be exactly similar in form to that in Fig. 3. The magnitude of the possible errors involved must again be emphasised. This point is also brought out by the last column in table V. It is improbable that the value of α, after approximating to the "ideal" figure of $366{\cdot}5 \times 10^{-5}$ in concentrated solutions, should fall and fluctuate in the dilute solutions, as the experimental figures appear to indicate.

The free energies of dilution of sodium chloride at 25° from saturated solution to 1·0N and from 1·0N to 0·1N have been calculated by Rodebush (*loc. cit.*) from freezing-point measurements to be respectively 2477 and 2464 calories.

Our value for $-\Delta F_{298}$ from 1·0N to 0·1N can be obtained from column four of table VIII, and is $10590/4{\cdot}189 = 2528$ cals., a rather higher figure. A saturated solution of sodium chloride at 25° is 5·43N, and contains 6·14 molecules per 1000 grams of water (as against 5·41N and 6·12 molecules per 1000 grams at 18°). If we extrapolate to this concentration on Fig. 2, we obtain the value 2·0279 for the electromotive force in volts of the experimental cell at 25°. From this figure and that for the cell with saturated solution at 18°, we calculate for the reaction

$$2Na \text{ (in form of 0·1389 per cent. amalgam)} + Hg_2Cl_2 \longrightarrow 2Hg + 2NaCl \text{ (solid)}$$

that $-\Delta F_{298}$ is 195,775 joules and $-\Delta H_{291}$ is 196,585 joules, in both cases for the transformation of 1 gram-equivalent. From this value of $-\Delta F_{298}$ and from $-\Delta F_{298}$ for a 1·0N-solution (table IV, column three), we calculate that $-\Delta F_{298}$ from saturated solution to 1·0N is $11{,}110/4{\cdot}189 = 2652$ calories, a much higher figure than that of Rodebush.

The difference of the above value of $-\Delta H_{291}$ for the reaction

involving the production of solid sodium chloride and that of $-\Delta H_{291}$ for the reaction involving the production of saturated sodium chloride solution (see table IV) furnishes us with the heat of solution of one molecule of sodium chloride in a saturated solution at 18°. This value comes to 195,000—196,585 joules, or −378 calories. There are no experimental determinations with which this figure can be directly compared. Using the van't Hoff isochore, and taking the solubility of sodium chloride as 35·79 grams and 35·92 grams per 100 grams of water at 18° and 25° respectively, we calculate the heat of solution as −89·5 calories, a far smaller value. The assumption of the validity of the gas laws, however, involved in this equation is certainly not justified, and we believe our value to be nearer the truth.

If we compare the values deduced from our curve for heats of solution in given quantities of water and for heats of dilution with experimental values, the concordance is only moderate. For the heat of solution of one molecule of sodium chloride in 9·2 molecules of water, Stackelberg (Landolt-Börnstein, "Tabellen," 4th edition, p. 875) found −410 calories; for the same in 10 molecules of water, van Deventer and van de Staat (*Zeitsch. physikal. Chem.*, 1892, **9**, 55) found −475 calories. We deduce, respectively, −371 and −373 calories. For the heat of solution of one gram-molecule of sodium chloride in 100 gram-molecules of water, Thomsen (Landolt-Börnstein, "Tabellen," 4th edition, p. 875), Stackelberg (*Zeitsch. physikal. Chem.*, 1898, **26**, 545), and van Deventer and van de Staat found, respectively, −1180 calories, −1030 calories, and −1130 calories. Our value is −1110 calories. When, however, we compare the different values for heats of dilution over concentration limits included in this range, the discrepancies are large. We get much smaller heat effects for dilution up to concentrations of one molecule of sodium chloride to 20 molecules of water, and much larger for dilutions between $1NaCl:50H_2O$ and $1NaCl:100H_2O$. Thus van Deventer and van de Staat found the molar heat of dilution from $1NaCl:10H_2O$ to $1NaCl:20H_2O$ to be −247 calories, whereas our figure is −17 calories. Similarly, their value for dilution from $1NaCl:50H_2O$ to $1NaCl:100H_2O$ is −128 calories per mol. NaCl. Our value is −463 calories.

The Reaction $2Na + Hg_2Cl_2 \longrightarrow 2NaCl + 2Hg$.

Lewis and Kraus (*loc. cit.*) found that 0·2062 per cent. amalgam at 25° is 0·8456 volt positive to metallic sodium, whilst the temperature-coefficient of the electromotive force of the combina-

tion is $-0{\cdot}0000408$ volt/degree. It follows that the amalgam is 0·8459 volt positive to sodium at 18°.

The measurements in tables I and II show that our amalgam (*c*) is 0·0068 volt positive to (*b*) at 18°, and that (*b*) is 0·0110 volt positive to (*a*). At 25°, the potential differences are 0·0069 and 0·0114 volt respectively. Plotting these figures and interpolating to find the relative potentials of the 0·2062 per cent. amalgam at these two temperatures, we obtain the result that it is negative to the amalgam (*c*) (0·1389 per cent.) by 0·01465 volt at 18° and 0·01495 volt at 25°. Combining these values with the figures of Lewis and Kraus, it follows that amalgam (*c*) is positive to sodium by 0·86055 volt at both 18° and 25°. From the electromotive forces of the cells, amalgam (*c*) | saturated NaCl | Hg_2Cl_2 | Hg, experimentally determined for 18° and extrapolated for 25°, we calculate for the cell

$$Na \mid \text{saturated NaCl} \mid Hg_2Cl_2 \mid Hg$$

that

$$e_{291} = 2{\cdot}88865 \text{ volts},$$
$$e_{298} = 2{\cdot}88845 \quad ,,$$

and for the cell reaction

$$2Na + Hg_2Cl_2 \longrightarrow 2NaCl \text{ (solid)} + 2Hg$$

that

$$-\Delta F_{291} = 66{,}573 \text{ calories}$$
$$-\Delta F_{298} = 66{,}569 \quad ,,$$
$$-\Delta H_{291} = 66{,}740 \quad ,,$$

per gram-equivalent transformed. The "calorimetric" value of $-\Delta H_{291}$ is obtained by subtracting the accepted heat of formation of $\frac{1}{2}Hg_2Cl_2$ (Varet) from the heat of formation of NaCl (Thomsen), that is, 31,315 from 97,700, leading to a figure of 66,385 cals.

Free Energy in Solution of One Molecule of Sodium Chloride.

By adding to the above values of $-\Delta F$ for the reaction

$$2Na + Hg_2Cl_2 \longrightarrow 2NaCl + 2Hg$$

the values of $-\Delta F$ for the reaction

$$2Hg + Cl_2 \text{ (one atmosphere)} \longrightarrow Hg_2Cl_2,$$

that is, 25,255 and 25,125 cals. per gram-equivalent at 18° and 25° respectively (Ellis, *loc. cit.*, p. 757), we arrive at once at values for the difference in free energy between sodium and chlorine on the one hand and solid sodium chloride on the other, namely, for the reaction

$$Na + \tfrac{1}{2}Cl_2 \text{ (one atmosphere)} \longrightarrow NaCl \text{ (solid)}.$$

$$-\Delta F_{291} = 91{,}828 \text{ calories},$$
$$-\Delta F_{298} = 91{,}694 \quad ,,$$

As a check on these values, we can calculate $-\Delta H_{291}$. The value found is 97,400 cals., whilst the calorimetric value already referred to above is 97,700 cals.

We are now in a position to state the values of the free energy of one molecule of sodium chloride at different dilutions in aqueous solution, taking the free energies of the two elements concerned, sodium and chlorine, as zero. The figures are contained in table X, and are obtained by combining the above values for the free energy of solid sodium chloride with the figures in table VIII and the value deduced on p. 1032 for $-\Delta F_{298}$ from saturated to 1·0*N*-sodium chloride. Similar figures for the total energy of a molecule of sodium chloride could also be calculated, but the data are not regarded as sufficiently trustworthy.

TABLE X.

C in mols. per litre (saturated).	Free energy of 1 mol. of NaCl in calories at 18°.	25°.
3·0	−91828	−91694
1·0	−92956	−92858
0·5	−94401	−94346
0·1	−95154	−95128
0·02	−96863	−96874
0·01	−98568	−98580
	−99292	−99314

Activities of Ions and Undissociated Molecules.

From the data contained in table V, activity ratios can be calculated by the method given on p. 1022. This has been done, and the results are contained in table XI.

TABLE XI.

C in mols. per 1000 grams of water.	Activity $NaCl_c$ / Activity $NaCl_{0\cdot1003}$		Activity Na_c^+ / Activity $Na_{0\cdot1003}^+$		Activity of Na^+ (assuming value in 0·1003 solution is 0·073 at 25°).	Thermodynamic degree of dissociation.
	18°.	25°.	18°.	25°.	25°.	25°.
6·12	6096·0	6249·0	78·1	79·05	5·771	0·94
3·196	867·0	874·4	29·44	29·57	2·159	0·67
1·022	70·8	71·7	8·414	8·468	0·618	0·60
0·5034	19·29	19·15	4·392	4·376	0·319	0·63
[0·1003	1·0	1·0	1·0	1·0	0·073	0·73]
0·02003	0·0522	0·0560	0·229	0·237	0·0173	0·86
0·01001	0·0149	0·0162	0·122	0·127	0·0093	0·93

From the ratios in columns two to five, and assuming with Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461) that the most

likely value for the ionic activity of such an electrolyte as sodium chloride in 0·1*N*-solution is 0·073, the values in columns six and seven are calculated. The term "thermodynamic degree of dissociation" to denote the ratio of ionic activity to total concentration seems preferable to "activity coefficient," as used by Ellis (*loc. cit.*). The latter term should be retained for expressing the ratio activity/concentration for the same molecular species, according to the nomenclature introduced by Lewis.

This table shows that the thermodynamic degree of dissociation first falls off as the concentration of the dissolved sodium chloride increases from 0·01*N*, passes through a minimum value at about 1*N*, and then increases to the high figure of 0·94 at the saturation point. This behaviour is shared qualitatively by aqueous hydrogen chloride and potassium chloride solutions. The former show a marked minimum for the value of the thermodynamic degree of dissociation at about 0·5*N* (Ellis, *loc. cit.*), whilst for potassium chloride solutions the lowest value lies at about 2*N* (Harned, *J. Amer. Chem. Soc.*, 1916, **38**, 1986).

Lithium chloride solutions have not yet been investigated over a sufficient range to discover a minimum, supposing one to exist.

Our values for this function can be compared with those obtained by Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461) from measurements of sodium chloride concentration cells with transference. His figures are given in table XII, and the agreement with ours is seen to be good.

TABLE XII.

C of NaCl in mols. per litre.	Activity. $T=25°$.	Thermodynamic degree of dissociation.
3·0	2·261	0·754
2·0	1·397	0·698
1·0	0·628	0·628
0·5	0·312	0·624
0·3	0·192	0·64
[0·1	0·073	0·73]

The value of 0·0093 for the activity of the sodium ion in 0·01*N*-solution, obtained on the assumption that the activity in 0·1*N*-solution is 0·073, is identical with that assumed by Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 2601) for the activity of the potassium and hydrogen ions in 0·01*N*-solutions. His assumption leads to ionic activities for these ions in 0·1*N*-solutions of 0·078 and 0·082 respectively, figures considerably higher than the corresponding one for the sodium ion. If, however, we calculate the activity of the lithium ion in 0·1*N*-solution from the results of

Pearce and Mortimer (*loc. cit.*), assuming that the activity in 0·01*N*-solution is 0·0093, we arrive at a figure of 0·070, still lower than that for sodium ions. The fact that the relative degrees of hydration of the four ions in question arrange themselves in the inverse order of magnitude to that of the activities in 0·1*N*-solution may be of significance.

Owing to the present lack of suitable viscosity data to apply to the existing conductivity measurements, no attempt can be made to calculate accurately the activity coefficients of the ions and undissociated molecules. It is, however, certain that, starting from dilute solutions, a/c for the ions at first decreases, passes through a minimum, and then increases, whilst a/c for the undissociated molecules increases throughout, and reaches very high values in concentrated solutions. Sodium chloride in this respect acts in a similar way to other electrolytes.

The different points of view from which the anomalies of strong electrolytes can at present most fruitfully be discussed are dealt with in the excellent papers of Bates, Pearce and Mortimer, Harned and others, already referred to, and there is no need to add anything here, particularly as there are still many gaps in absolutely necessary data unfilled.

Molecular Condition of Sodium in Sodium Amalgams.

Our experiments furnish an interesting confirmation of the work of Ramsay (T., 1889, **55**, 533) and of Cady (*J. Physical Chem.*, 1898, **2**, 551), who found by vapour pressure and electrometric experiments, respectively, that sodium, dissolved in mercury at concentrations varying from 0·03 to 0·66 per cent., behaved as if it were giving an abnormally large number of osmotically active particles, that is, as if simple atoms were dissociated into something simpler. From table II, it will be seen that the electromotive forces between amalgams (*a*) and (*b*), if measured in a sodium chloride solution at 25°, would amount to 0·0114 volt, and between (*b*) and (*c*) to 0·0069 volt. Substituting these values and those for the concentrations of the amalgams in the equation

$$e = \frac{2{\cdot}303\,RT}{F}\,\frac{1}{x}\,.\log\frac{c_1}{c_2}$$

where x represents the association factor of the metal atoms dissolved in the mercury, we find for the combination amalgam (*a*)–amalgam (*b*) that x is 0·68, and for the combination amalgam (*b*)–amalgam (*c*) that x is 0·65. These values for x correspond with apparent molecular weights of 15·6 and 15·0 respectively. Ramsay,

working at high temperatures, found that the apparent molecular weight decreased as the concentration of sodium increased. For concentrations closely corresponding with ours, values of about 18 were obtained. Cady, working at 19—20°, and measuring amalgam concentration cells, using pyridine solutions as electrolytes, obtained figures from 11·3 to 16·3, again decreasing with increasing concentration of amalgam.

At first sight, it would seem possible that sodium atoms dissolved in mercury are dissociated into sodium ions and free electrons (the latter surrounded by a condensed atmosphere of mercury molecules), and that the electrical conductivity of sodium amalgams is partly electrolytic in nature. Such a state of affairs would be analogous to that shown by Kraus (*J. Amer. Chem. Soc.*, 1908, **30**, 1323) to exist in solutions of sodium in liquid ammonia. Skaupy (*Zeitsch. physikal. Chem.*, 1907, **58**, 560), indeed, has tried to prove that the supposed equilibrium

$$\text{metal} \rightleftharpoons \text{metal ion} + \text{electron}$$

in dilute amalgams obeys the Ostwald dilution law. The experiments of Lewis, Adams, and Lanman (*J. Amer. Chem. Soc.*, 1915, **37**, 2656) are, however, completely against this assumption. They showed that, when a current passes through a sodium amalgam solution, the sodium concentrates at the positive pole. Their suggested explanation is rendered less probable by subsequent very exact experiments by Hine (*ibid.*, 1917, **39**, 882) on the conductivity of dilute alkali metal amalgams, but it is at all events clear that the dissolved sodium is not associated with a surplus positive electric charge.

The true explanation of the apparent low molecular weights is in all probability the formation of compounds between the sodium and the mercury. The importance of taking this into account was first pointed out by Haber (*Zeitsch. physikal. Chem.*, 1902, **41**, 399). Sodium and mercury can combine to form the well-defined compound $NaHg_6$. Abegg ("Handbuch," II, i, 679) has shown that it is a likely assumption that the concentration of free mercury in the amalgams is thereby lowered to a sufficient extent to explain Ramsay's (and also the electrometric) results. Cady (*loc. cit.*) has further demonstrated that the abnormalities in the electrometric results disappear if the heat of dilution of the amalgams is taken into account. Actually measuring this for sodium amalgam between certain concentrations, he obtained very exact agreement. Low apparent molecular weights are associated with abnormally high electromotive forces for concentration cells, with positive heats of dilution, and with the formation of exothermic compounds.

Those interested are referred to papers by Richards and Garrod-Thomas (*Zeitsch. physikal. Chem.*, 1910, **72**, 165), and by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 501), where the situation is clearly set out.

The temperature-coefficients of our own cells were measured over too small a range to allow of the calculation from them of the heats of dilution of the sodium amalgams used.

Summary.

(1) Measurements of cells of the type

$$Hg|Hg_2Cl_2 \text{ aqueous NaCl solutions}|\text{sodium amalgam}$$

have been carried out at 18° and 25° for concentrations of sodium chloride ranging between 0·01*N* and saturated solution.

(2) From these have been calculated the free and total energies of dilution of sodium chloride between the concentration limits referred to.

(3) The transport number of the sodium ion in different dilute sodium chloride solutions has been calculated.

(4) The molecular heat of solution of sodium chloride in saturated solution at 18° has been calculated.

(5) The changes in free and total energies of the reactions

$$2Na + Hg_2Cl_2 \longrightarrow 2NaCl\ (\text{solid}) + 2Hg,$$
$$2Na + Cl_2\ (1\ \text{atmosphere}) \longrightarrow 2NaCl\ (\text{solid}),$$

have been calculated.

(6) The free energies of one molecule of sodium chloride in aqueous solution at various concentrations at 18° and 25°, referred to the free energies of the elements sodium and chlorine as zero, have been calculated.

(7) The "thermodynamic degrees of dissociation" of sodium chloride in aqueous solution at different concentrations at 25° have been calculated, together with the corresponding activities of the sodium ion.

(8) Confirmation has been obtained of previous work on the molecular condition of sodium in sodium amalgams.

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LXXXIX.—*The Active Substance in the Iodination of Phenols.*

By Victor Cofman.

Numerous methods are known for the preparation of iodophenols, and the entrance of iodine in the molecule has been accounted for in various ways. The object of this communication is to prove that hypoiodous acid is solely responsible for the iodination in a number of processes investigated, and to show that the presence of the above-mentioned substance as an intermediate compound satisfactorily explains the formation of iodophenols by the various known methods.

That hypoiodous acid has the property of reacting with phenols, producing iodo-substituted compounds, is no new discovery. Selivanov (*Ber.*, 1894, **27**, 1012) pointed out that the iodination of phenol by means of nitrogen iodide is due to the hydrolysis of the latter compound and the consequent production of hypoiodous acid; various other authors (Bray, *Zeitsch. physikal. Chem.*, 1906, **54**, 563; Cohn and Schultz, *Ber.*, 1905, **38**, 3294; Gardner and Hodgson, T., 1909, **96**, 1822) have suggested that the same compound may be responsible for the formation of iodophenols by the "iodine and alkali" methods, but no definite proofs have been adduced in support of this view, nor has it yet been attempted to ascribe the production of iodophenols in all the known instances to the presence of one and the same substance in the various reacting mixtures.

The earliest mention of any iodophenol is that made by Piria (*Compt. rend.*, 1843, **18**, 187), but the merit of a first investigation of this class of compounds rests with Lautemann (*Annalen*, 1861, **120**, 299), who prepared several iodophenols and iodosalicylic acids. From his method of preparation, Lautemann inferred that, on heating iodine with salicylic acid, a direct substitution takes place, although he could not explain what happened to the displaced hydrogen.

Later, Kekulé (*Annalen*, 1864, **131**, 221) showed that the compounds obtained by Lautemann's process were formed only when the mixture of iodine and salicylic acid was dissolved in alkalis. He prepared the same compounds by the action of iodine and iodic acid on salicylic acid, and explained their formation thus:

(i) $C_7H_6O_3 + I_2 + KOH = C_7H_5O_3I + KI + H_2O$.
(ii) $5C_7H_6O_3 + 2I_2 + HIO_3 = 5C_7H_5O_3I + 3H_2O$.

Kekulé's opinion was that iodine has the property of displacing the hydrogen atoms of certain organic compounds in the presence of a third substance capable of oxidising, or removing in some other fashion, the hydriodic acid formed during the reaction. This explanation has since been put forward to account for the formation of iodophenols by other methods, namely, (i) the "iodine and mercuric oxide" method (*Ber.*, 1872, **5**, 380); (ii) the "iodine and sodium phosphate" method (*J. Pharm. Chim.*, 1902, [vi], **15**, 217); (iii) the iodine monochloride method (*ibid.*).

According to this view, in every one of the above cases, the first part of the reaction is $HR + I_2 = IR + HI$ (where R = phenolic radicle), and the second part consists in the removal of the hydriodic acid thus formed by the third substance present.

The production of iodo-substituted compounds by means of iodine monochloride was originally given a similarly simple interpretation (Brown, *Phil. Mag.*, 1854, [iv], **8**, 201):

$$HR + ICl = IR + HCl.$$

A more complicated equation was put forward by Dagener (*J. pr. Chem.*, 1879, [ii], **20**, 324) as representing the course of the reaction in his hypochlorite method of obtaining tri-iodoresorcinol:

$$6CaOCl_2 + 12KI + 12HCl + 2C_6H_4(OH)_2 = 6CaCl_2 + 6HI + 12KCl + 2C_6HI_3(OH)_2 + 6H_2O,$$

whilst in the "dry" reactions of Birnbaum (*Ber.*, 1882, **15**, 459) and Schall (*Ber.*, 1883, **16**, 1897), the authors assume that the hydrogen atom displaced by the iodine wanders in one case to the carboxyl, and in the other to the hydroxyl group, thus:

$$OH\cdot C_6H_4\cdot CO_2H + I_2 = OH\cdot C_6H_3I\cdot CO_2H + AgI$$

and

$$C_6H_5\cdot ONa + I_2 = C_6H_5\cdot OI + NaI,$$
$$C_6H_5\cdot OI \longrightarrow C_6H_4I\cdot OH.$$

Finally, Willgerodt (*J. pr. Chem.*, 1888, [ii], **37**, 446) supplied for his method the equation

$$C_6H_5\cdot OH + NI_3 = C_6H_2I_3\cdot OH + NH_3.$$

Experimental.

The opinion that the formation of iodophenols must be due to the presence of hypoiodous acid suggested itself to the present author during the preparation of di-iodosalicylic acid by the action of iodine monochloride on salicylic acid. It was observed, on the one hand, that the reaction did not take place in the absence of

water, whilst, on the other hand, an aqueous solution of iodine monochloride soon lost its power of combining with salicylic acid. The gradual disappearance of the "active iodine" (that is, iodine capable of attacking the phenolic molecule) from such a solution is strikingly shown in the table given below. The method employed was to add 10 c.c. of a solution of iodine monochloride in glacial acetic acid (Wijs' solution) to 100 c.c. of water; the mixture was allowed to remain at the ordinary temperature (12°) for the specified time, after which excess of sodium salicylate (5 c.c. of a 10 per cent. solution) was added to combine with the "active iodine"; this was followed after one minute by the addition of an excess of potassium iodide and titration with $N/10$-thiosulphate solution.

Table showing the Rapid Decrease in the Amount of "Active Iodine" Present in Aqueous Iodine Monochloride Solution.

Time solution was allowed to remain.	No. of c.c. of $N/10$-thiosulphate required.	"Active iodine."
0	0	27·8
10 sec.	4·1	23·7
20 ,,	5·8	22·0
30 ,,	7·3	20·5
1 min.	10·5	17·3
2 ,,	13·3	14·5
3 ,,	16·8	11·0
5 ,,	17·1	10·7
10 ,,	18·1	9·7
30 ,,	20·2	7·6
1 hr.	21·9	5·9
2 hrs.	23·3	4·5
16 ,,	25·1	2·7
24 ,,	26·2	1·6

How is this rapid decrease in the activity of iodine monochloride solutions explained? As is well known, iodine monochloride is partly hydrolysed in aqueous solution,

$$ICl + H_2O \rightleftharpoons IOH + HCl,$$

the hypoiodous acid formed quickly decomposing into iodic acid and free iodine, the reaction being usually represented thus:

$$5IOH = 2I_2 + HIO_3 + 2H_2O.$$

Now, it is highly probable that the decrease in the activity of the solution is due to this decomposition of the hypoiodous acid, but, owing to our imperfect knowledge of the constitution of iodine monochloride solutions, this cannot be definitely proved. Other products of decomposition, such as the compound ICl,HCl and

iodine trichloride, are present, and these may have a bearing on the matter.

Nevertheless, it is quite clear that the present view, which ascribes the iodination of phenols in iodine monochloride solution to the action of the iodic acid formed, is untenable, since the amount of iodophenol produced actually diminishes as the concentration of iodic acid and free iodine increases.

The next step was to investigate the formation of iodophenols in alkaline iodine solutions. In this case, thanks to the fact that the kinetics of the system iodine–potassium iodide–sodium hydroxide has been fully investigated by Schwickler (*Zeitsch. physikal. Chem.*, 1895, **16**, 303), Forster (*J. Physical Chem.*, 1903, **56**, 324), Bray (*Zeitsch. physikal. Chem.*, 1906, **54**, 563), and Skrabal (*Monatsh.*, 1907, **28**, 217; 1909, **32**, 167, 815), it is possible to show that, in such solutions, *the mass of "active iodine" is at any instant equal to the amount of hypoiodous acid present*, thus proving them conclusively to be one and the same substance.

Without going too deeply into the kinetics of hypoiodite solutions, it may be stated that the first reaction which takes place when iodine is dissolved in alkalis, namely,

$$I_2 + OH' \rightleftharpoons IOH + I',$$

attains rapidly a state of equilibrium and, in strongly alkaline solutions, the concentration of free iodine is negligible. The decomposition of the resulting hypoiodous acid, on the contrary, is relatively slow, proceeding with measurable velocity. It has thus been found possible to prove that the reaction is one of the second order, the rate of change being expressed by the empirical formula

$$-\frac{d[IOH]}{dt} = \frac{[I'] + e(E)}{[OH']} \cdot ka[IOH]^2,$$

where E = total concentration of electrolytes and e = a variable factor depending on the concentration of I' and OH'.

Under special experimental conditions (when $OH'/I' < 10$), the member $e(E)$ of the equation becomes negligibly small, and the simpler formula

$$-\frac{d[IOH]}{dt} = \frac{[I']}{[OH']} \cdot [IOH]^2,$$

expresses the rate of change.

In the experiments which follow, the initial concentration of iodine ions and hydroxyl ions was twenty times greater than that of the hypoiodous acid, so that, despite the fact that hydroxyl ions

are used up and iodine ions formed during the reaction, the ratio [I′]/[OH′] remained practically constant.

The method of procedure was as follows: Two hundred c.c. of a $N/50$-iodine solution (in potassium iodide) were rapidly mixed with an equal volume of $0{\cdot}4N$-sodium hydroxide solution, so that the concentration of the mixture was (in mols. per litre)

$$0{\cdot}005\mathrm{I}_2 + 0{\cdot}2\mathrm{NaOH} + 0{\cdot}2\mathrm{KI}.$$

Successive quantities of this solution (20 c.c. each) were removed after the specified time; excess of phenol (3 c.c. of a 5 per cent. solution) was added to combine with the "active iodine," the mixture acidified with acetic acid, and the iodine thus liberated (from the iodate and iodide) was titrated with $N/10$-thiosulphate.

Two explanatory remarks are here needed:

(i) The reaction between phenol and "active iodine" in the presence of excess of the former is very rapid. This may be seen by simply adding phenol to a freshly prepared solution of iodine in alkali; the yellowish-green colour of the latter immediately disappears. The speed of the reaction was also proved by allowing phenol to act for various lengths of time (from 0·5 to 20 minutes) on solutions of equal "active iodine" content; the amount of iodine used up was the same, irrespective of the time allowed before acidifying.

(ii) It is essential that acetic acid or some other weak acid is employed for acidifying the mixture. If a strong mineral acid is used, then iodine is liberated from the iodate and iodide present before the whole of the hydroxyl ions have been neutralised; hypoiodous acid is consequently formed and acts on the phenol, causing an apparent increase in the amount of "active iodine." This phenomenon was first described by Kekulé, and its effect on the estimation of hypoiodous acid was later eliminated by saturating the solution with carbon dioxide before acidifying (Batey, *Analyst*, 1911, **38**, 132). If acetic acid is used, the treatment with carbon dioxide becomes unnecessary; this was proved by means of blank experiments on a mixture of sodium iodate and iodide in the presence of phenol.

In the table below, the third column gives the amount of "active iodine" in terms of c.c. of $N/100$-iodine solution; k_1, k_2, and k_3 are constants corresponding with reactions of the first, second, and third order respectively, that is,

$$k_1 = \frac{1}{t_2 - t_1} \cdot \log \cdot \frac{c_1}{c_2}; \quad k_2 = \frac{c_1 - c_2}{(t_2 - t_1)c_1c_2}; \quad k_3 = \frac{1}{2(t_2 - t_1)} \cdot \frac{1}{c_2^2} - \frac{1}{c_1^2}$$

Table showing the Velocity of Decomposition of the "Active Iodine Compound" in Alkaline Solution.

Time.	C.c. of $N/100$-thiosulphate required.	c = "active iodine."	10^2k_1	10^3k_2	10^4k_3
0	0	19·5	—	—	—
1 min.	2·0	17·5	4·20	5·8	3·15
2 ,,	3·7	15·8	4·43	6·14	3·65
3 ,,	5·0	14·5	3·73	5·67	3·8
5 ,,	7·4	12·1	4·43	6·84	5·35
8 ,,	10·1	9·4	3·66	7·90	7·5
10 ,,	11·3	8·2	2·96	7·78	8·9
14 ,,	13·0	6·5	2·52	7·96	11·0
18 ,,	14·1	5·4	2·01	7·83	13·4
25 ,,	15·2	4·3	1·41	6·80	14·1
30 ,,	15·8	3·7	1·30	7·53	19·0
40 ,,	16·5	3·0	0·91	6·31	19·1
60 ,,	17·3	2·2	0·67	6·01	23·8
90 ,,	18·7	1·5	0·53	7·07	39·7
			Mean 10^3k_2 =	6·90	

The temperature of the solution remained approximately constant (10·3—10·7°) throughout the experiment.

It will be seen from the foregoing table that whilst k_1 and k_3 vary considerably, k_2 remains satisfactorily constant over a wide range of concentration, thus proving the decomposition of the "active substance" to be a bimolecular reaction, just as is the case with hypoiodous acid; the occurrence of a maximum in the value of the constant is also suggestive of the decomposition of hypoiodous acid, and, finally, k_2 as above determined can be shown, after applying the necessary corrections, to have the same value as the constant obtained by other authors for the rate of decomposition of hypoiodous acid.

Thus, Skrabal (*Monatsh.*, 1911, **32**, 171), working at 20·2° with alkaline iodine–potassium iodide solutions of the same concentration as employed above, obtained for the constant of the rate of decomposition of hypoiodous acid (k'_2) the mean value $2·63 \times 10^3$. Two corrections are needed to make the constant found for the "active substance" comparable with that obtained by Skrabal, namely, (i) a correction for the difference in the amount of solution analysed, and (ii) a correction for the difference in the temperature.

(i) From the equation

$$k_2 = \frac{c_1 - c_2}{(t_2 - t_1)c_1c_2}$$

it is easily seen that k_2 is inversely proportional to the quantity of solution analysed at a time. As this was 89·49 c.c. in Skrabal's

case, whilst the present author used only 19·5 c.c., the first correcting factor for the constant will be $\frac{19{\cdot}5}{89{\cdot}49}$.

(ii) The temperature-coefficient of the constant was found by Skrabal to be 2·1 (per 10°). Now, k_2 was determined at 10·5° and k'_2 at 20·2°, a difference of 9·7°, hence the second correcting factor for the constant is $\frac{2{\cdot}1 \times 9{\cdot}7}{10}$.

Applying these two corrections, we obtain

$$k_{2(\text{corrected})} = 6{\cdot}90 \times \frac{19{\cdot}50}{89{\cdot}49} \times 2{\cdot}1 \times \frac{9{\cdot}7}{10} \times 10^3$$
$$= 3{\cdot}06 \times 10^3.$$

The agreement between the two constants is good, bearing in mind that the "mean value" (that is, the arithmetical mean) of the constants made use of in the above calculations is only a rough approximation to their true value.

Having thus proved that the iodine which combines with the phenol in alkaline solutions is present as hypoiodous acid, and having shown that there is strong evidence for assuming that the same compound is the active substance in iodine monochloride solutions, other methods used in the preparation of iodophenols may be examined. A close scrutiny will show that in most, if not all, the processes by which these compounds are obtained, hypoiodous acid is an intermediate product.

(1) "*Iodine and Mercuric Oxide*" *Method*.—The formation of hypoiodous acid from these two substances in the presence of water is a matter of common knowledge (Köne, *Ann. Phys. Chem.*, 1845, [ii], **66**, 300; Taylor, *Chem. News*, 1897, **76**, 22).

(2) "*Hypochlorous Acid and Potassium Iodide*" *Method*.—The interaction between hypochlorous acid and potassium iodide, resulting in the formation of hypoiodous acid, has been studied by Klimenko (*Zeitsch. physikal. Chem.*, 1897, **23**, 552, 558) and confirmed by Bray (*ibid.*, 1906, **54**, 563). We may therefore substitute for Dagener's complicated formula the following:

$$C_6H_4(OH)_2 + 3IOH = C_6HI_3(OH)_2 + 3H_2O.$$

(3) "*Iodine and Iodic Acid*" *Method*.—The reaction

$$5IOH \rightleftharpoons 2I_2 + HIO_3 + 2H_2O$$

is a reversible one, and the continuous removal of hypoiodous acid by the phenol causes it to proceed towards the left.

(4) "*Iodine and Sodium Phosphate*" *Method*.—Iodine dissolves

in a solution of disodium hydrogen phosphate, the simplest way of formulating the reaction being

$$Na_2HPO_4 + I_2 + H_2O \rightleftharpoons NaH_2PO_4 + NaI + IOH \quad . \quad . \quad (i)$$

The hypoiodous acid thus formed decomposes further,

$$5IOH \rightleftharpoons HIO_3 + 2I_2 + H_2O \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

so that, finally, hypoiodous acid is in equilibrium on the one hand with iodine and sodium phosphate, and on the other with iodine and iodic acid. The following experiment confirms this view.

A solution of iodine and disodium hydrogen phosphate in water was prepared and allowed to remain for a fortnight, so that equilibrium was attained; the solution was still of a red colour, showing that free iodine (or, more correctly, I'_3) was present. To one portion of this solution phenol was added, which combined with the "active iodine" and decolorised the solution; the mixture was then immediately acidified, and the iodine liberated from the iodide and iodate present was titrated with $N/100$-thiosulphate. Another portion of the same solution, after adding phenol, was allowed to remain for twenty-four hours before acidifying and titrating as above. The amount of iodine used by the phenol was in both cases the same. This is exactly what is to be expected from the equations put forward above; the addition of phenol removes the hypoiodous acid present, thus disturbing both equilibria, but, since reaction (i) has a far greater velocity than reaction (ii), practically the whole of the free iodine combines with the sodium phosphate, leaving the iodate ion unaffected.

The reaction between iodine and disodium hydrogen phosphate is formulated in a rather different way by Skrabal and Gruber (*Monatsh.*, 1916, **37**, 543), who give the equation

$$3I_2 + 6HPO''_4 + 3H_2O = 5I' + IO'_3 + 6H_2PO'_4,$$

but it is obvious from the result of the above experiment that this equation does not represent the actual state of affairs; for, if it did, since the reaction is a balanced one, the removal of the free iodine by the phenol (supposing this to be possible without the intermediate formation of hypoiodous acid) would cause the reaction to proceed towards the left until no more iodate ion remained in solution. This, however, is not the case, for, as we have seen, the iodate remains unaffected by the removal of the "active iodine."

(5) *Nitrogen Iodide Method.*—Selivanov (*loc. cit.*) proved that this compound yielded hypoiodous acid on hydrolysis, and sug-

gested that the iodination is due to the last-mentioned substance. He gave the following equations:

$$NI_3 + 3H_2O = NH_3 + 3IOH,$$
$$3IOH + 3C_6H_5{\cdot}OH = 3C_6H_4I{\cdot}OH + 3H_2O.$$

(6) Passing on to the "dry" reactions of Birnbaum and Schall, we see that even here the formation of hypoiodous acid is not excluded. A very small quantity of moisture would be sufficient, since the water used up in the first part of the reaction is regenerated at the end. Thus in Schall's method

$$C_6H_5{\cdot}ONa + I_2 + H_2O = C_6H_5{\cdot}OH + NaI + IOH,$$
$$C_6H_5{\cdot}OH + IOH = C_6H_4I{\cdot}OH + H_2O,$$

and in Birnbaum's

$$OH{\cdot}C_6H_4{\cdot}CO_2Ag + I_2 + H_2O = OH{\cdot}C_6H_4{\cdot}CO_2H + AgI + IOH,$$
$$OH{\cdot}C_6H_4{\cdot}CO_2H + IOH = OH{\cdot}C_6H_3I{\cdot}CO_2H + H_2O.$$

This new way of formulating the reactions obviates the necessity of assuming any intramolecular change. It should be further noted that Kekulé's criticism of Lautemann's method applies also to the last-mentioned reaction; in all probability, the formation of iodosalicylic acid does not take place on heating iodine with silver salicylate, but during the subsequent treatment. In any case, the preliminary heating is quite superfluous; if to a suspension of silver salicylate in alcohol is added a solution of iodine (in alcohol), the colour of the latter disappears quickly at first, the reaction becoming slower as the ratio between silver salicylate and iodine added approaches unity. After removing excess of iodine by shaking with mercury and filtering, there is obtained, on evaporating the alcohol, a mixture of iodosalicylic acids.

The theory that the formation of iodophenols is due to the action of hypoiodous acid is thus seen to explain the preparation of those compounds by many different methods. The real test for a useful theory, however, is its capability of predicting new phenomena and suggesting fresh lines of research. It will be seen that the above theory stands this test.

(i) For instance, it is evident that on the above theory any method of obtaining hypoiodous acid could also be used for the preparation of iodophenols; thus, it can be predicted that iodophenols will be formed by the action of silver carbonate or sulphate and iodine on phenols.

(ii) The converse proposition, that any method of preparing iodophenols may be made to yield hypoiodous acid, is probably

also true. This has been shown to be the case in the iodine and sodium phosphate method of Richard.

(iii) A further successful line of research suggested by the present theory, namely, the estimation of hypoiodous acid, will be dealt with in a later paper.

So far, the hypoiodous theory of iodination has been applied to phenolic compounds only, but many of the methods for the preparation of iodophenols, such as Kekulé's (iodine and iodic acid) and Weselsky's (iodine and mercuric oxide), have been successfully used in introducing iodine atoms into other organic compounds. Again, the formation of iodoform from alcohol and from acetone has been proved to be due to hypoiodous acid (Daventer and van't Hoff, *Rec. trav. chim.*, 1888, **1**, 35; Pieroni, *Gazzetta*, 1912, **42**, i, 534). It will be seen from this that hypoiodous acid as an iodinating agent has a much wider range than that outlined above. Its formation might possibly explain the action of concentrated sulphuric and nitric acids, ferric chloride, etc., as iodine carriers (Neumann, *Annalen*, 1887, **241**, 84; Meyer and Schwalb, *ibid.*, 1885, **231**, 195; Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1917, **39**, 441).

Throughout this paper, the term "hypoiodous acid" has been employed to denote the compound IOH, although, so far as its properties are concerned, "iodine hydroxide" would be a more suitable term. The latter name has been avoided, as it suggests the existence of positive iodine ions, which many chemists regard with suspicion. The work of Walden (*Zeitsch. physikal. Chem.*, 1903, **43**, 385) on the conductivity of iodine in inorganic solvents, as well as other considerations (Abegg and Auerbach, "Handbuch d. anorg. Chem.," IV, (ii), 455), lend, nevertheless, considerable support to the view that iodine cations do exist. If this be really the case, then the previous statement may be modified to: the formation of iodophenols, and that of hypoiodous acid, is brought about by the presence of positive iodine ions.

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XC.—*The Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium.*

By Edward Bradford Maxted.

The activation of hydrogen by metallic catalysts is undoubtedly intimately connected with the phenomenon of occlusion; indeed, hydrogenation reactions which proceed in the presence, for instance, of palladium and free hydrogen, may also be effected by palladium containing hydrogen in the occluded state.

From this point of view the factors that determine the catalytic activity of various preparations of a given metal for hydrogenation reactions should include the occlusive power of the preparation for hydrogen, and it should follow, as a necessary sequence, that substances which exert an inhibitive effect on catalytic activity will also inhibit the occlusive power.

For the purpose of the present paper, hydrogen sulphide has been taken as a typical catalyst poison, palladium being chosen as the occluding material by reason of its high absorptive power for hydrogen.

It may be mentioned, with reference to the influence of other catalytically poisonous substances on the occluding power of palladium for hydrogen, that De Hemptinne (*Zeitsch. physikal. Chem.*, 1898, **27**, 249) noticed that palladium which had been treated with carbon monoxide lost its absorptive power for hydrogen, at any rate at low temperatures. Carbon monoxide was afterwards found by Paal and Hartmann (*Ber.*, 1910, **43**, 243) to inhibit the activity of this metal for the catalytic reduction of sodium picrate. The latter authors, together with Steyer (Paal and Hartmann, *Ber.*, 1918, **51**, 711; Paal and Steyer, *ibid.*, 1743), showed also that mercury acts similarly on palladium hydrosols.

In the work about to be described the hydrogen-occluding power of oxygen-free palladium-black was measured before and after treatment with hydrogen sulphide, and, incidentally, data were obtained relating to the absorption of hydrogen sulphide by palladium and the stability of the absorption compound.

Experimental.

The apparatus employed consisted of a small glass absorption pipette containing a known weight of palladium-black and connected by means of capillary glass tubing to a Sprengel pump and

to a gas burette respectively. This gas burette, which contained mercury, was provided with a three-way cock for the introduction of gas. The various parts of the apparatus were joined by fusion, and all stopcocks were mercury-sealed. In order to prevent access of mercury vapour to the palladium, short plugs of aluminium turnings, preceded and followed by glass-wool, were inserted in the system on each side of the absorption pipette.

The palladium was prepared in the apparatus itself by the reduction of palladium chloride at 100° by means of electrolytic hydrogen, from which the last traces of oxygen had been removed by treatment with palladinised asbestos at 350°, followed by soda-lime.

According to the measurements of Mond, Ramsay, and Shields (*Proc. Roy. Soc.*, 1897, [*A*], **62**, 290), palladium-black occludes about 873 volumes of hydrogen at the ordinary temperature and pressure. The ease and rapidity with which this is given up varies somewhat with the nature of the palladium, but, in any case, the bulk is evolved in a vacuum at 100°. The greater part of the hydrogen occluded is taken up at once, but a slight additional absorption takes place on allowing the palladium to remain in hydrogen.

In order to avoid the possibility of changing the nature, and especially the catalytic activity, of the palladium-black by overheating, it was decided, in the present case, to regard 100° as the maximum temperature to which the palladium should be subjected, this temperature being, as already stated, sufficiently high for the extraction by exhaustion of practically the whole of the occluded hydrogen.

The first point to be studied was the constancy of the volume of hydrogen which could be removed by exhaustion at 100° or, alternatively, occluded by exposing palladium, which had been dehydrogenated in this way, to the action of fresh hydrogen at the ordinary temperature. In order to ensure uniformity in the experimental conditions, the system was in every case exhausted to a standard pressure of 3 mm. at 100°, and exhaustion was continued as long as any appreciable quantity of gas was being evolved under these conditions, the hydrogen being collected over mercury in the usual way. Subsequently, a known volume of hydrogen was admitted to the absorption tube from the gas burette and the contraction read off, the volume of the absorption pipette, including its connexions, having been determined previously.

Table I summarises the results of eight experiments carried out in this way. The measurements numbered 5 and 6, also those numbered 7 and 8, were made with fresh quantities of palladium-black, which in every case weighed 0·6 gram, corresponding with

1 gram of palladium chloride. The volume of gas evolved or occluded is in every case reduced to normal temperature and pressure.

TABLE I.

No. of expt.	Vol. of hydrogen evolved on exhaustion. C.c.	Vol. of hydrogen subsequently occluded. C.c.
1	41·3	40·0
2	40·2	40·5
3	41·9	41·1
4	41·4	—
5	41·5	40·6
6	41·9	—
7	41·6	40·5
8	41·5	—

The average volume of hydrogen evolved or occluded under the above conditions is thus about 41 c.c., corresponding with 68·5 c.c. per gram of palladium.

Dry hydrogen sulphide, prepared by the action of heat on a solution of magnesium hydrosulphide, was now allowed to pass into the exhausted reaction tube in place of hydrogen and to remain in contact with the palladium, from which the occluded hydrogen had previously been removed by exhaustion at 100°. Occlusion of a certain amount of the gas took place at once, and was followed by a slower and continuous absorption of a secondary nature. It had previously been ascertained that hydrogen sulphide, provided it is dry and free from oxygen, does not attack either mercury or aluminium at a rate sufficient to influence the measurements.

Table II summarises an absorption experiment with 0·6 gram of palladium.

TABLE II.

Time.	Vol. H_2S absorbed. C.c. at N.T.P.
1 min.	6·2
5 min.	7·1
10 „	7·5
3 hr. 20 min.	10·4
18 hr.	12·2
40 „	13·5

By interrupting the absorption after a suitable time of contact, palladium containing various proportions of hydrogen sulphide could be obtained. The hydrogen sulphide thus absorbed was not removed to any great extent by exhaustion at the ordinary temperature, this being especially the case when the hydrogen sulphide content of the palladium was comparatively low, and, on passing hydrogen into the

exhausted absorption pipette, occlusion of this gas no longer took place.

Under the conditions employed, it was not found possible, in view of the velocity of the primary occlusion of hydrogen sulphide by palladium, to prepare specimens of the metal containing less than about 13·5 c.c. of hydrogen sulphide per gram, corresponding with an absorption of about 8 c.c. for the 0·6 gram of palladium taken for each experiment, and the minimum volume of hydrogen sulphide required for the total inhibition of the hydrogen-occluding properties of palladium could therefore not be determined. This figure is, however, certainly less than 14 c.c. per gram of palladium.

On exhausting the palladium containing hydrogen sulphide at 100° a volume of gas, approximately equal to that of the hydrogen sulphide contained in the preparation, was evolved, but was found on analysis to consist almost entirely of hydrogen, the sulphur of the absorbed gas being retained by the palladium.

Table III records three results of this nature.

TABLE III.

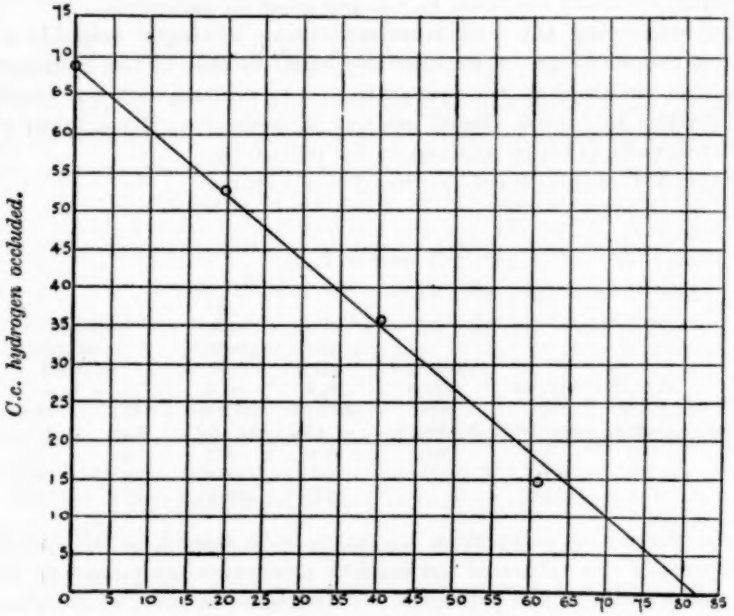
No. of expt.	Wt. of Pd in grams.	Vol. of H_2S absorbed.	Occlusive power for hydrogen.	Vol. of gas evolved in a vacuum at 15°.	Vol. of gas subsequently evolved in a vacuum at 100°.	Analysis of total gas evolved	
						H_2. C.c.	H_2S. C.c.
1	0·6	8·2	Nil.	0·1	8·2	8·3	—
2	0·6	13·5	,,	1·1	12·8	13·7	0·2
3	0·6	17·7	,,	2·3	16·4	17·4	1·3

An interesting observation was made with respect to the specific influence of the nature of the sulphur absorption compound on the occlusive power of the palladium for hydrogen, in that, whilst about 8 c.c. of hydrogen sulphide are sufficient to inhibit completely the occlusive power for hydrogen of 0·6 gram of palladium, the equivalent quantity of sulphur, which remains behind after exhaustion at 100°, is by no means sufficient to prevent completely the occlusion of hydrogen.

In order to study quantitatively the influence of sulphur in the latter form, measurements were made of the volume of hydrogen which was capable of being absorbed or evolved by various specimens of palladium of known sulphur content, the hydrogen portion of the absorbed hydrogen sulphide having been previously extracted by exhaustion at 100°.

The results obtained are tabulated below, the measurements of occlusive power having been carried out under similar conditions to

the experiments recorded in table I. The sulphur content was determined both by measuring the volume of hydrogen sulphide which had been absorbed, subtracting any small quantity evolved as such during the preliminary exhaustion at 100°, and also, as a check, after measuring its occlusive power, by dissolving the preparation in aqua regia and precipitating as barium sulphate. In order to obtain a preparation containing as high a proportion of sulphur as 0·0328 gram to 0·54 gram of palladium, corresponding with an absorption of 23·0 c.c. of hydrogen sulphide, an absorption period of about three weeks was necessary.



Sulphur content in milligrams.

TABLE IV.

No. of expt.	Wt. of Pd. Gram.	Wt. of sulphur content. Gram.	Occlusive power for hydrogen. Vol. absorbed. C.c. at N.T.P.	Occlusive power for hydrogen. Vol. subsequently evolved. C.c. at N.T.P.
1	0·6	0·0117	31·7	31·6
2	0·6	0·0117	31·8	32·4
3	0·6	0·0117	31·3	31·0
4	0·6	0·0117	30·7	—
5	0·6	0·0242	21·2	21·6
6	0·54	0·0328	8·4	8·2
7	0·54	0·0328	8·0	7·9
8	0·54	0·0328	7·7	7·9

On plotting the above results graphically, it will be seen that the mean occlusive power for hydrogen is approximately a linear function of the sulphur content, and that each atom of sulphur renders almost exactly four palladium atoms incapable of occluding hydrogen, the remainder of the palladium being capable of occluding normally. The accompanying curve, which shows this relation, refers to 1 gram of palladium.

Whilst any discussion respecting the constitution of the compound formed by the decomposition of hydrogen sulphide by palladium does not fall within the scope of the present paper, it may be noted that the occlusive power of a preparation of this kind may be predicted by assuming a compound Pd_4S to be formed, and ascribing to the residual palladium its normal power of absorption. There is, however, insufficient evidence to justify the assumption of the actual formation of this or any compound, and it may be mentioned in this connexion that palladium foil was found to remain untarnished by pure dry hydrogen sulphide both at the ordinary temperature and at 100°.

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WALSALL, STAFFS.

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XCI.—*The Critical Solution Temperature of a Ternary Mixture as a Criterion of Purity of Toluene.*

By KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES.

THE use of binary critical solution temperatures in the determination of purity has become well known since Crismer (*Bull. Soc. chim. Belg.*, 1895, **9**, 145; 1896, **10**, 312; 1904, **18**, 1; 1906, **20**, 294) originally demonstrated the great delicacy of the critical solution temperature of the alcohol–petroleum binary in detecting the presence of, and in estimating the amount of, water in the alcohol. As a means of distinguishing rapidly between various fats and oils and of testing the purity of liquid substances, the use of critical points has been considerably developed. The occurrence, however, of the critical points of binary mixtures in convenient ranges of temperature is relatively rare, and hence the applicability of the method is for practical purposes comparatively limited.

This disadvantage largely disappears in a ternary mixture. If

a ternary mixture is used, a far wider field of stable organic liquids is available as constituents; by adjusting the composition of the mixture of liquids chosen, the critical points can be brought into a convenient range of temperature.

The objection which has been mainly urged against a ternary mixture for this purpose (Timmermans, *Zeitsch. physikal. Chem.*, 1907, **58**, 129) is the great accuracy with which the constituents must be measured in making up the mixture, and, as a result, the definite use of a ternary mixture has received no application in the laboratory as a criterion of liquid purity. On the other hand, a considerable number of miscibility points of systems virtually ternary, or of a higher order, have been suggested as rough qualitative methods in industrial work (compare Salamon and Seaber, *J. Soc. Chem. Ind.*, 1915, **34**, 461; Shrewsbury, *Analyst*, 1909, **34**, 348; 1914, **39**, 529; Armani and Rodano, *J. Soc. Chem. Ind.*, 1912, **31**, 912 (abstract); Tortelli and Fortini, *Gazzetta*, 1911, **41**, i, 173; Fryer and Weston, *Analyst*, 1918, **43**, 3; Parkes, *ibid.*, 82). In a strictly binary mixture, commonly no fine adjustment of the proportions of the two constituents is necessary in order to find the temperature of the critical solution point.

Industrial toluene, which has passed through a full process of purification by treatment with sulphuric acid and so forth, and careful rectification, may yet contain a certain proportion of admixture, which may be taken to consist in the main of paraffin hydrocarbons of like boiling point (compare recent papers on allied subjects by various authors, *J. Soc. Chem. Ind.*). The toluene distils completely within 0·5°, but its density is about 0·23 per cent. lower than that of pure toluene.

In this investigation, we have had as an object the establishing by means of a change in the critical solution temperature ("c.s.t.") of a ternary mixture a general criterion of the purity of toluene, and specifically to detect and to estimate petroleum in toluene.

Toluene will give a ternary c.s.t. with many solutions, as, for example, certain aqueous alcohol, aqueous acetone, aqueous acetic acid, etc., the temperatures of critical solution of which lie in convenient ranges when the proportion of water is rightly chosen. The best solution for this purpose will have the following characteristics: It must be stable under ordinary conditions, and its composition accurately and conveniently determined; the two components of the solution must be easily obtained pure; and the critical-point phenomena must be distinct.

Aqueous acetic acid and toluene form a ternary mixture which meets the conditions just laid down, the c.s.t. of which can by proper choice of the proportion of water be brought into the region

of 0—50°. Unlike formic acid, which with benzene gives a binary c.s.t. at 73·2° (Ewins, T., 1914, **105**, 350), anhydrous acetic acid, propionic acid, and *n*-butyric acid are completely miscible with benzene and toluene at the ordinary temperature.

Waddell (*J. Physical Chem.*, 1898, **2**, 232) examined the ternary mixture benzene–acetic acid–water at 25° and 35°, which, as would be expected, very closely resembles the system toluene–acetic acid–water. Both are very similar to the system chloroform–acetic acid–water (Wright, *Proc. Roy. Soc.*, 1891, **49**, 174; 1892, **50**, 375).

In a ternary as in a binary mixture, the sensitiveness of the critical points to impurity in one constituent of the mixture is determined by the relative solubility of the impurity and the one constituent in the other constituents of the mixture. Thus, the remarkable delicacy of Crismer's method is to be attributed to the great difference of solubility of the water and alcohol in petroleum. Hence the effect of an impurity in the toluene is various, depending on the relative solubilities of the impurity and toluene in the acetic acid solution. Thus we find that the presence of benzene leads to a relatively small fall in the temperature, of xylene to a relatively small rise. The fall in temperature is approximately a linear function of the concentration of benzene, and the rise of that of xylene. With a given aqueous acetic acid (water = 10·1 per cent., m. p. 2·77°), when the proportions of the two constituents are 0·6232 c.c. of aqueous acetic acid and 0·4958 c.c. of the other (see later), the critical solution temperatures are:

TABLE I.

	c.s.t.
Benzene	−3·3°
Toluene	23·6°
m-Xylene	52·9°
Bromobenzene	34·5°
p-Bromotoluene	65·4°

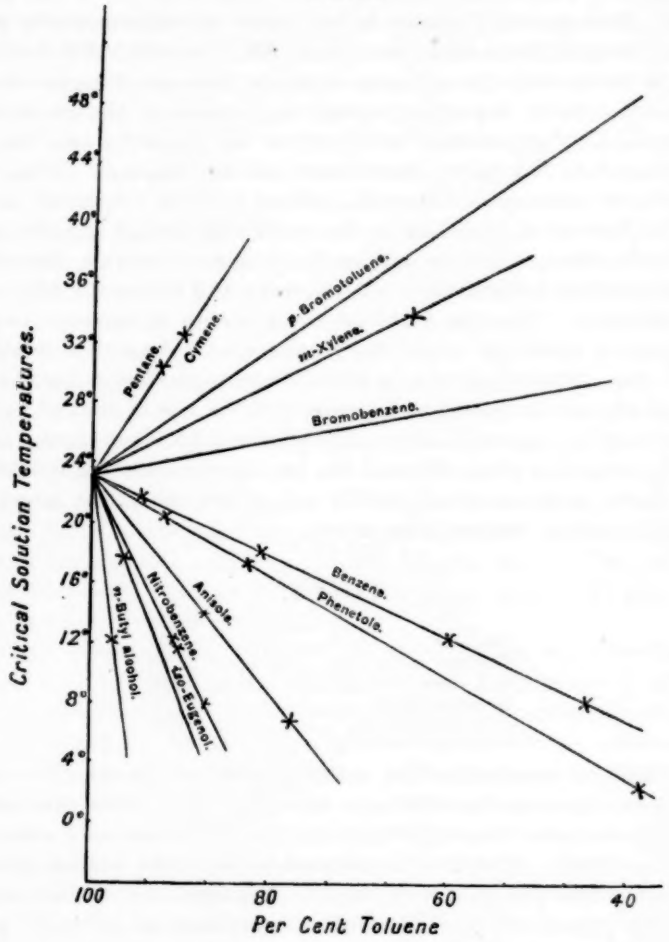
It will be noted that the melting point of benzene is a surer guide to the presence of toluene than the c.s.t. One per cent. of toluene depresses the melting point by 0·6°, but only raises the c.s.t. by 0·27°. The c.s.t. is comparable with the melting point in detecting the presence of xylene in benzene. In the absence of melting points, the critical solution temperatures are good guides to the presence of xylene in toluene, and vice versa.

Other substances with a greater solubility in water than benzene have a still greater depressing effect on the c.s.t.; to the presence in toluene of such relatively soluble substances as *iso*amyl and *n*-butyl alcohols, the c.s.t. becomes extremely sensitive, and is greatly depressed by small quantities. The curves shown in Fig. 1

will sufficiently illustrate the effect of various substances which we have examined.

The solubility of paraffin hydrocarbons in acetic acid and in water is very much less than that of toluene. The presence of petroleum raises, therefore, the c.s.t. of the systems toluene–acetic

FIG. 1.



acid–water and benzene–acetic acid–water in a very marked way. If the toluene contains 1 per cent. of petroleum (b. p. 124—132°, octane), the c.s.t. (23·5°) is raised by 1·6°. Since the temperature of critical solution can be read with certainty to 0·1° at the range of temperature used, such small proportions as one-sixteenth per

cent. of paraffin can be detected in benzene, toluene, xylene, and the like, and the proportion estimated to the same degree of accuracy. For paraffin in benzene, the method is far more delicate than the melting point. The fact that the same aqueous acetic acid can be used in the three hydrocarbons named is an additional advantage.

In the homologous series of paraffin hydrocarbons, the solubilities are very similar, but the progressive decrease of solubility as the series is ascended in the effect on the c.s.t. of the toluene–acetic acid–water system is obvious (table II).

TABLE II.

Substance present as impurity in toluene.	Elevation or depression of c.s.t. for 1 per cent. of substance.
Benzene	−0·27°
Xylene	0·29°
Cymene	0·90°
Pentane	0·90°
Hydrocarbon fractions mainly b. p. 109–110° ...	1·4°
(Octane) 124–132° ...	1·6°

If it be assumed that the complete substitution of octane for toluene is accompanied by a proportional rise in the c.s.t., the c.s.t. of pure octane with this particular aqueous acetic acid will be about 160°. Since increase in the concentration of the acetic acid solution used lowers the temperature of critical solution, it appears probable that some paraffin hydrocarbons would give binary critical solution temperatures with more concentrated—glacial—acetic acid. We have determined (approximately) the values of certain fractions.

TABLE III.

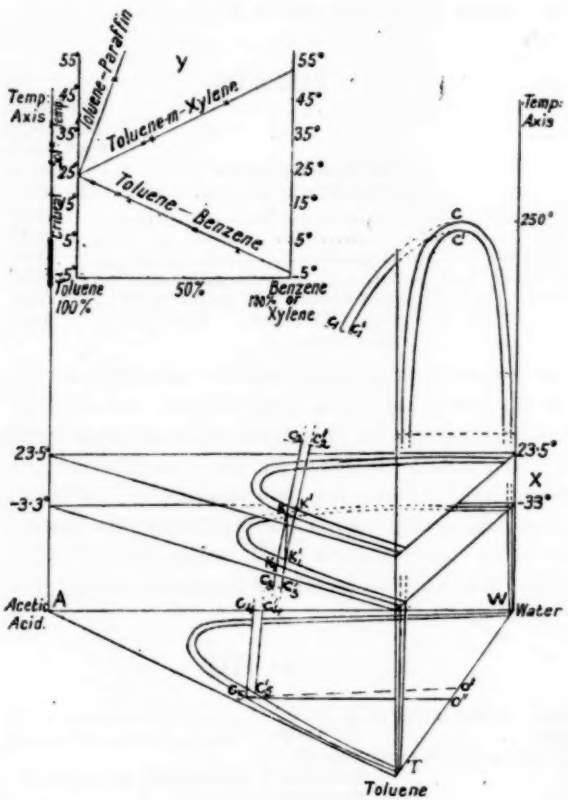
			c.s.t.
Hexane.	Acetic acid, m. p. 15·6°	.....	1°
Hexane.	,, ,, 15·0°	.....	25°
Hydrocarbons boiling at 205–225°	Acetic acid, m. p. 16·15°		59°
,, ,, 225–240°			66·5°
,, ,, 240–264°			81·0°

This similarity in solubility relation among the homologous fatty paraffins, which is the cause of this small difference in the values of the c.s.t., may be contrasted with the widely varying relations among the fatty acids.

In Fig. 2 (in which we have followed Roozeboom, "Heterogene Gleichgewicht," Vol. III.), $CC_1C_2C_4C_5$ represents the critical curve of the system toluene–acetic acid–water from the binary c.s.t. of

toluene–water, C (which we find to lie approximately at 250°, under pressure), through the ternary c.s.t.'s on the isothermal binodal curves; the base of the prism corresponds with an isothermal just below 0°. Similarly, $C'C'_1C'_2C'_3C'_4C'_5$ represents the corresponding critical curve for benzene. In the enlarged inset (X), K and K' represent the ternary c.s.t.'s of the toluene and benzene systems, respectively, at the isothermal 23·5°, whilst K_1 and K'_1 represent the c.s.t.'s at −3·3°.

FIG. 2.



The percentage composition of the system at K is: toluene, 39·34; acetic acid, 54·52; water, 6·14.

The percentage composition of the system at K'_1 is: benzene, 39·72; acetic acid, 54·22; water, 6·06.

Waddell's values for the benzene system at 25° are: benzene, 39·6; acetic acid, 54·22; water, 7·6.

If in a system the composition of which is represented by K the

toluene is gradually displaced by the same volume of benzene, the critical phenomenon exhibited by the system remains always distinct up to the complete replacement of toluene, that is, KK'_1, a line parallel to the temperature axis, cannot be detected as having left the region of the critical curve. The great similarity in the solubility relations of benzene and toluene would account for this behaviour. Moreover, the temperature of the (now) quaternary c.s.t. is linearly related to the increasing proportion of benzene in the system (inset *Y*, Fig. 2). Quite analogous results were found to hold in the case of xylene, the critical curve being as much without that of toluene as that of benzene within, and also, as the diagram (*Y*) shows, replacement of toluene by xylene causes a linear corresponding alteration in the c.s.t.

On the other hand, the critical curves of aqueous acetic acid–petroleum and aqueous acetic acid–toluene, owing to the greater difference in solubility, lie very much further apart. It is probable that in cases of this kind, substitution of petroleum for toluene would lead the system away from the curve, but up to 17 per cent. of petroleum the critical phenomena remain very distinct, and the relation between the proportion of petroleum and the elevation of the c.s.t. is linear (Fig. 6).

Relation between Melting Point of the Acetic Acid and the c.s.t. with Toluene.

The c.s.t. of the ternary system toluene–acetic acid–water rises proportionally to the increase in the quantity of water over a small range—3·5 per cent. and the elevation of the c.s.t. is almost linearly related to the depression of melting point of the acetic acid (Table IV, and Fig. 3.)

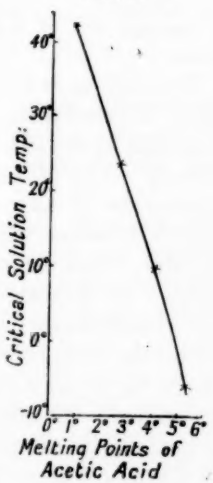
TABLE IV.

M.p. of aqueous acetic acid.	Percentage of water.	c.s.t.
5·45°	8·2	−5·9°
4·2°	9·0	9·8°
2·77°	10·1	23·5°
0·9°	11·7	41·9°

(The percentage of water is obtained from Faucon's numbers, *Ann. Chim. Phys.*, 1910, [viii], **19**, 84).

Similarly, the c.s.t. of the binary system alcohol–petroleum (Crismer) and benzene–formic acid (Ewins) rises proportionally to the concentration of water added.

FIG. 3.



In Fig. 2, let C_5 represent the critical point on the lowest binodal curve, ATW; on replacing acetic acid by water, keeping the proportion of toluene constant, the composition of the system follows the line CO'' parallel to the acetic acid–water line, AW. CO', the projection of the critical curve on the isothermal plane, represents the whole series of critical compositions up to the binary c.s.t. of toluene and water. Hence, unless O' approximates to O'' in position (assuming CO' to be a straight line), addition of water soon takes the system away from the region of the critical curve. The phenomenon of critical solution, then, will not appear when the temperature of miscibility is observed. It must be emphasised that in our experiments the distance travelled by the system as water replaces acetic acid, along CO'', is relatively very small. The system is still found sufficiently near to the critical curve for an obvious exhibition of the critical phenomena.

Measurement of the Constituents.—In using the change in the c.s.t. of a ternary mixture produced by an impurity for the purpose of estimating the impurity, such as we are suggesting, accuracy of measurement of the quantity of the constituents is of the greatest importance (compare Timmermans, *loc. cit.*). Thus, as an illustration, the numbers given in the table of the temperature of the critical solution of the system toluene–acetic acid–water show the effect of an increase in the proportion of toluene (pure) of less than 1 per cent.

TABLE V.

Aqueous acetic acid.	Toluene.	Difference.	c.s.t.	Difference.
0·6232	0·5006	0·0144	24·05°	1·65°
0·6232	0·4862	0·0144	22·4°	

The difference 1·65° would correspond with the presence of 1 per cent. of petroleum.

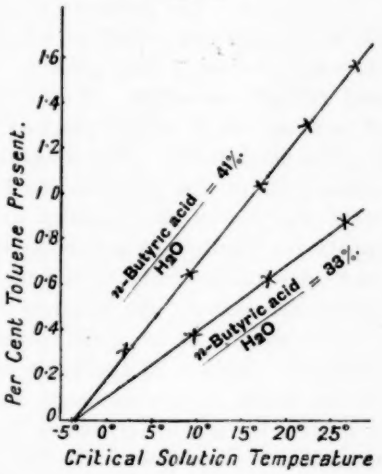
In the figure (2), the point K'_1 represents the composition of the ternary c.s.t. of benzene–acetic acid–water. Any change in the proportion of any one constituent causes the composition of the system to move either into a region of heterogeneity within the binodal curve or of unsaturation and homogeneity without the curve. In systems such as benzene–acetic acid–water (or toluene–acetic acid–water), the solubility relations of which change slowly with alteration of temperature, a considerable temperature change would be required before the miscibility point of the new system is reached. In other words, the sensitiveness of the c.s.t. to slight variations in composition is a consequence of the great extension of the figure along the temperature axis.

The very great importance of accuracy of proportions of the

constituents in a binary as well as in a ternary mixture is well illustrated by a perhaps extreme case which we have observed. Fig. 4 shows the effect of addition of toluene to two mixtures of *n*-butyric acid and water, one containing 41 and the other 33 per cent. of the acid. These two mixtures both give the same miscibility temperature (−3·7°) in the critical region, owing to the long, flat top of the solubility curve (Faucon, Rothmund, *Zeitsch. physikal. Chem.*, 1908, **63**, 57, and Timmermans). The solubility curve of the system alcohol–petroleum has a similar form.

If one regards the toluene as an impurity in the binary system butyric acid–water, each curve (Fig. 4) may be taken to show the effect of increasing concentration of the impurity on the binary c.s.t. If, however, it is desired to estimate by the elevation of the c.s.t the proportion of impurity, it will be seen that it is obviously essential that the proportions in which the constituents are taken shall be exactly known. If the proportion of *n*-butyric acid is 41 per cent., then the presence of 1 per cent. of toluene causes a rise in the c.s.t. of 21° (Fig. 4), whereas if the proportion of *n*-butyric acid is 33 per cent., 1 per cent. of toluene gives a rise of 35°.

FIG. 4.



Alternatively, let the concentration of toluene be fixed at 1 per cent., then a variation of the proportion of butyric acid from 41 to 33 per cent. will lead to a change in the c.s.t. of 15°. Yet in the absence of toluene both acid–water mixtures will have the same miscibility temperature.

This example brings out very clearly the necessity of using exact proportions of the constituents when the binary c.s.t. is being used as a criterion of the degree of purity. Only when the liquid is finally purified are the exact proportions of less importance, since before that stage is reached the system is not binary, but of a higher order. Thus, in the use which is commonly made of the alcohol–petroleum binary to *estimate* the proportion of water in the alcohol, it is essential, even for small quantities of water, that certain definite proportions of petroleum and aqueous alcohol should be used.

It is obviously of first importance, if the method is to become of practical utility, that the proper degree of accuracy should be combined with rapidity and simplicity of manipulation. We find that a remarkably high degree of accuracy can be reached by using small, carefully constructed pipettes, one for the solution of fixed concentration and the other for the liquid the purity of which is to be tested. The manipulation and the method of estimating petroleum in toluene which we recommend have been tested in the analytical laboratory of a large chemical works, and have received a very favourable report as giving accurate and consistent results in the hands of the average manipulator.

Experimental.

Apparatus.—The accurate measurement of (1) the solution used, (2) the liquid the purity of which is to be tested, is the first consideration in using this method. Weighing of liquids is a lengthy and difficult operation. We find that for small volumes the degree of accuracy which can be reached with properly constructed pipettes is quite remarkable. The diagram (Fig. 5) shows the form and the dimensions of the pipettes we have used. The essentials in the form and use of the pipettes are as follows: (1) The tip of the pipette is drawn into a fine capillary tube, so that the liquid may be held with certainty to the mark, whilst the time for delivery is about one minute for volumes 0·5—1 c.c. (2) The stem of the pipette should be of small diameter, since with wide tubes, (*a*) change in pressure of the finger causes a very appreciable variation in the height of the meniscus, an effect which is very marked with a pipette having an ordinary tip; (*b*) error in adjustment of the meniscus is magnified. (3) After drawing in a liquid and adjusting to the mark, the outside of the tip should be gently wiped with a silk duster, at the end of which operation the liquid fills the pipette from the mark to the end of the tip. (4) When the pipette has ceased delivering, the capillary tip (in contact with the glass) is emptied by a gentle blow. (5) Every care is taken to have a clean glass surface; finally, the pipette is washed out with distilled water and dried by a current of dust-free air.

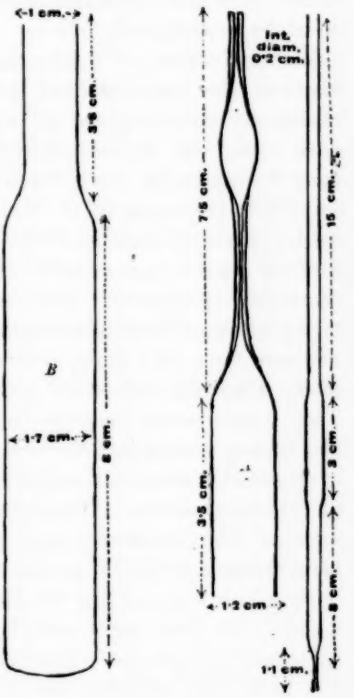
The following illustrations will emphasise the extremely small error entailed in the use of these pipettes. A "5 c.c." pipette, terminating in a fine capillary tube, delivered its content of water in two minutes. At a definite temperature, it delivered in five successive trials 4·95979 c.c., 4·95986 c.c., 4·95995 c.c., 4·95966 c.c., 4·96011 c.c.; the volumes are calculated from the weights of water delivered. It will be seen that the maximum variation between

any two readings is 0·00045 c.c., and the maximum variation from the arithmetic mean 0·00024 c.c., or 0·005 per cent.

A "2 c.c." pipette, which delivered its content of water in only ten seconds, lengthened, however, in delivery to one minute, gave the following weights of water in five successive experiments: 2·0146, 2·0146, 2·0172, 2·0138, 2·0172 grams. Here the maximum variation reaches 0·0034 gram, and from the arithmetic mean is 0·0017 gram, or 0·08 per cent.

A very small pipette, of the same type, but smaller than those we have generally used, delivering its content of water very slowly—in about one minute—gave the following readings in four successive experiments: 0·2524 c.c., 0·2524 c.c., 0·2525 c.c., 0·2527 c.c. The maximum variation between any two readings is 0·0003 c.c., and from the arithmetic mean 0·0002 c.c., or 0·1 per cent.

Fig. 5.



We have used small pipettes of various content, but for the apparatus in which we have observed the c.s.t. of the toluene–aqueous acetic acid and similar systems, pipettes of from 0·4 to 0·7 c.c. capacity are required. The aqueous acetic acid pipette delivered 0·6232 c.c., and the toluene pipette 0·4958 c.c. These are the quantities of our aqueous acetic acid (see later) and pure toluene, which we found to exhibit the phenomena of critical solution in the clearest and most obvious way. The maximum variation from the mean is 0·0002 c.c., and hence in one pipette the maximum error may amount to 0·03 per cent., and in the other to 0·04 per cent. An error of measurement of 0·001 c.c., that is, five times the actual maximum variation observed, produces a difference of 0·1° in the c.s.t. of toluene, and would correspond with an error of 0·0125 per cent. in the estimation of paraffin.

The experimental tube has the form and dimensions shown in the diagram (Fig. 5). The cap (*A*) is fastened on the tube (*B*) by a short piece of rubber tubing. This tube is attached to the

thermometer by rubber rings, and the whole combination is used as a stirrer of the bath.

The thermometer is a standard instrument, preferably graduated in twentieths, but a graduation in tenths will suffice for most purposes.

The bath is a glass beaker of 2 litres capacity filled with water and heated by a small gas burner of the Argand type. The flame is simply and effectively regulated by a screw clip compressing a rubber tubing; the adjustment is very delicate when the rubber and slip are made fast to the bench, and hence the temperature is raised with the deliberation necessary as the temperature of critical solution is attained.

Determination of c.s.t.—At the ordinary temperature, the contents of the experimental tube are in two layers, the lower layer being mainly composed of aqueous acetic acid. As the temperature rises, the mutual solubility of the two layers increases, and they intermingle more readily as their densities, viscosities, etc., approach the same value, the suspensions of one layer in the other taking place in smaller drops requiring longer to separate. Gradually, striations appear through the body of the liquid, which is now distinctly opalescent. The temperature of the bath should now be rising at the approximate rate of 1° in five minutes. The striations become more and more delicate as the layers approach identity in every respect, and faint beginnings of blue fluorescence appear. This fluorescence deepens in tone, and when evident throughout the liquid, the striations being still clearly visible, the temperature of the bath must be raised more slowly at the approximate rate of 0·1° per minute. Close observation will now show the disappearance of the striations and greatly increased fluorescence. This temperature is taken as the critical solution point. The clearness with which one can see the thermometer scale through the liquid is a good test (first mentioned by Rothmund, *loc. cit.*) for observation in these final stages. The reading can now be repeated by cooling the bath very slightly, say 0·2°, and again taking the critical solution temperature. Readings may be repeated as often as desirable with the same mixture.

Materials.—The pure acetic acid was fractionated through an eight-bulb still-head. A considerable quantity was placed in a special double-stoppered bottle, and water added to bring it to the composition desired. We have used two solutions containing approximately 10·1 and 11·7 per cent. of water, and melting approximately at 2·77° and 0·9° respectively. To obtain a correct reading of the melting points of such dilute acetic acids is a very difficult matter (compare Faucon, *loc. cit.*). The temperature

cannot be determined within 0·02—0·03°. The acid melting at "2·77°" gave a c.s.t. with pure toluene at 23·5°, and that melting at "0·9°" a c.s.t. at 41·9°. A difference in melting point of 0·01° of the acetic acid leads to a difference of the c.s.t. with pure toluene of 0·1°.

Since pure toluene can be readily obtained in quantity, it is better to prepare an aqueous acetic acid approximately of the desired composition, and then to determine the c.s.t. with pure toluene, rather than deduce the c.s.t. of the system from the melting point of the aqueous acetic acid.

Pure Toluene.—A quantity of toluene which had been prepared in the usual way from recrystallised toluene-*p*-sulphonic acid was shaken with saturated sodium carbonate solution, washed with distilled water twice, and dried over granulated calcium chloride (which does not, however, reduce the saturation point below 0° unless the liquid is simultaneously cooled). It was then fractionated through an eight-bulb still-head, and the large middle fraction refractionated. The "standard" toluene thus obtained has the characteristic that, on distillation, the first 10 c.c., the main fraction, and the last 10 c.c. yield the same c.s.t. with a given aqueous acetic acid. No change in the c.s.t. of the standard toluene could be observed after treatment with phosphoric oxide and refractionation.

The toluene has $D_{12\cdot6}^{12\cdot6}$ 0·87417; Perkin (T., 1896, **69**, 1241) gives $D_{12\cdot6}^{12\cdot6}$ 0·87403.

Benzene.—The benzene was obtained by fractionating a specimen (m. p. 5·4°) until the fractions (first, main, and final) gave a constant c.s.t. with the standard "acetic" acid melting at "0·9°," when quantities identical with those taken for toluene were used. The value of the c.s.t. is 14·3°. With acetic acid melting at "2·77°" the c.s.t. is −3·3°.

The Presence of Paraffin Hydrocarbons in Toluene.

For the purpose of studying the effect of the presence of paraffin hydrocarbons in toluene, the paraffin was obtained from American petroleum.

After shaking with sulphuric acid (95 per cent.) (which removes the olefines, Colman and Yeoman, *J. Soc. Chem. Ind.*, 1919, **38**, 57; Thole, *ibid.*, 39) until a fresh quantity of sulphuric acid remained uncoloured, the hydrocarbon was warmed and shaken with a mixture of nitric and sulphuric acids for many hours.

After washing with aqueous alkali and then with water, and drying with granular calcium chloride, it was distilled through an

eight-bulb still-head. After several fractionations, the two fractions, b. p. 109—110° and b. p. 124—132°, were used for admixture with toluene.

In determining the c.s.t. of the mixture, the pipette delivering 0·6232 c.c. was used for the aqueous acetic acid, and the pipette delivering 0·4958 c.c. for the mixture of toluene and petroleum. The results are summarised in the following table (VI) and graphically shown in Fig. 6.

TABLE VI.

A. Paraffin boiling at 124—132°. Aqueous acetic acid melting at "0·9°" and containing about 11·7 per cent. of water (Fig. 6).

Paraffin. Per cent.	c.s.t.	Paraffin. Per cent.	c.s.t.
0·0	41·8°	8·98	56·05°
1·054	43·65°	10·17	57·6°
1·31	43·9°	14·45	64·2°
2·08	45·4°	17·17	68·5°
3·926	48·1°		
6·17	51·4°		

B. Paraffin boiling at 109—110°. Aqueous acetic acid melting at "0·9°" and containing about 11·7 per cent. of water (Fig. 6).

Paraffin. Per cent.	c.s.t.
2·317	45·1°
4·09	47·5°
9·28	54·85°
14·54	62°

C. Paraffin boiling at 124—132°. Aqueous acetic acid melting at "2·77°" and containing 10·1 per cent. of water.

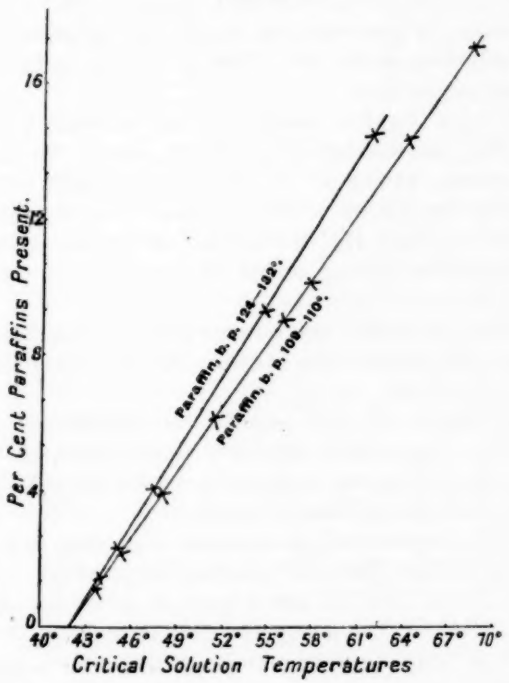
Paraffin. Per cent.	c.s.t.	Paraffin. Per cent.	c.s.t.
0	23·5°	6·17	33·05°
1·054	25·2°	8·98	37·6°
1·31	25·5°	10·17	39·0°
2·08	26·8°	17·17	50·1°
3·926	29·7°		

It is to be remarked that the presence of 1 per cent. of the paraffin boiling at 124—132° produces the same rise, 1·6°, in the c.s.t. whether aqueous acetic acid melting at "0·9°" or at "2·77°" is used.

Estimation of Petroleum in Industrial Toluene.

Several specimens of industrial toluene were examined, including some which had been purified to meet the Government standard, and boiled within 0·5°. Before determining the c.s.t., the toluene was shaken with small quantities of sulphuric acid (95 per cent.) until the acid no longer became coloured. It was then shaken with aqueous sodium hydroxide, washed with water, dried with calcium chloride, and fractionated through an eight-bulb still-head.

FIG. 6.



(The "Government" toluene gave a c.s.t. of 44·5° with "0·9°" acetic acid; a specimen of toluene of French official origin, a c.s.t. of 44·3°; and a specimen of toluene supplied by English distilleries, a c.s.t. of 44·0°.)

Three fractions were collected of the material which distilled within 0·5°, a small first fraction, a main fraction, and a small residue. The c.s.t.'s with aqueous acetic acid (m. p. "0·9°") were respectively 44·35°, 44·4°, and, with the residue, 45·2°, whereas pure toluene gives a value of 41·8°.

Thus but little elimination of impurity is effected by the fractionation; the c.s.t. of the 15 c.c. residue is only 0·8° above the main fraction, which has a value 2·6° above that of pure toluene. The chemical treatment and the fractionation would remove all impurity save paraffin hydrocarbons of similar boiling points, which, as is well known, are commonly found in the usual sources of toluene. The presence of xylene as the cause of the high value of the c.s.t., beyond a trace, is, apart from all else, completely excluded, inasmuch as an elevation of 2·6° would require from 8 to 9 per cent. of xylene (Fig. 2, *Y*).

If paraffin of about the boiling point 124—132° is taken as the main impurity, then, from the data given in the foregoing, the toluene contains 1·6 per cent. (by weight) of paraffins. If paraffin of about the boiling point 109—110° is the impurity, the toluene contains 1·85 per cent.

Some additional light is thrown on the problem by comparison of the densities, as the following results show. The specimen of industrial toluene, having a c.s.t. of 44·4°, has $D_{12\cdot4}^{12\cdot4}$ 0·8721. Pure toluene containing 1·6 per cent. of paraffin boiling at 124—132° has the same c.s.t. and $D_{12\cdot4}^{12\cdot4}$ 0·8718, whilst toluene containing 1·85 per cent. of paraffin boiling at 109—110° has again the same c.s.t. but $D_{12\cdot4}^{12\cdot4}$ 0·8710.

It may be inferred that the toluene contains somewhat less than 1·6 per cent. of paraffins, which distil over a range probably somewhat above 124—132°.

Direct estimation of the paraffin by Spielmann and Jones's (*J. Soc. Chem. Ind.*, 1917, **36**, 490) modification of Wilson and Roberts's method does not apparently give a very accurate result with such a small proportion of paraffin.

The paraffin was isolated in a similar way from a large volume of toluene distilling within 0·5°; it had $D_{14\cdot4}^{14\cdot4}$ 0·7312. The density of octane (b. p. 125·5°/760 mm.) is given as 0·7188 at 0°, and of nonane (b. p. 149·5°/760 mm.) as 0·733 at 0°.

We think it may be fairly claimed that the critical solution temperatures of aqueous acetic acid with industrial benzene, toluene, or xylene which have been fully purified afford an accurate means of determining the content of paraffin hydrocarbons.

We intend to pursue the study of ternary mixtures, and especially of the use of the critical solution temperatures of such mixtures as a criterion of purity of liquids.

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[*Received, July 22nd*, 1919.]

XCII.—*Thiocyanoacetone and its Derivatives and Isomerides.*

By Joseph Tcherniac.

Thiocyanoacetone, $SCN{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, was first obtained by the action of monochloroacetone on barium thiocyanate in alcoholic solution (Hellon and Tcherniac, *Ber.*, 1883, **16**, 349). Later it was found that the reaction takes place in the absence of alcohol when the crystallised barium salt is intimately mixed with monochloroacetone (Tcherniac, *Ber.*, 1892, **25**, 2623). Further investigation has shown that an aqueous solution of any thiocyanate of the alkalis (except that of ammonia) or of the alkaline earths can be used with advantage. As an example, the preparation by means of the sodium salt may be described.

To 92·5 grams (1 mol.) of monochloroacetone,* 191·4 c.c. (1·1 mols.) of a 46·55 per cent. solution of sodium thiocyanate were added, and the mixture was stirred for ten hours. The temperature rose about 25°, and a brown oil gradually separated. The whole product, oil and aqueous solution, was completely extracted with ether. The ethereal extract, which contained an appreciable quantity of dissolved thiocyanate, was shaken with successive quantities (10 c.c.) of water until the wash-water gave only a slight reaction with ferric chloride. The united washings, which contained some thiocyanoacetone, were reserved for addition to the following preparation before the ether extraction.

The ether was distilled off from a water-bath at the lowest temperature possible. Fifty c.c. of distilled water were added to the residue, and the whole was heated in a water-bath to 40—50° under 14 mm. pressure. The water distilled over, carrying with it some chloroacetone and its impurities, together with a very small quantity of thiocyanoacetone (0·35 gram).

The residue was dried in a vacuum over sulphuric acid, and analysis showed it to be nearly pure thiocyanoacetone (108—109 grams = 95 per cent. yield).

Purification of Thiocyanoacetone.—Thiocyanoacetone cannot be distilled without decomposition in the ordinary vacuum of the water-pump—about 14 mm. (Tcherniac, *Ber.*, 1892, **25**, 2625). It distils, however, unaltered under a pressure of about 1 mm. A portion of the thiocyanoacetone prepared as above was placed in an Anschütz distillation flask with collar and sealed-on receiver.

* Prepared by Fritsch's method (*Ber.*, 1893, **26**, 597), using magnesia instead of marble, and carefully fractionated. It contained traces only of dichloroacetone.

Ground in the neck of the receiver were a U-tube filled with calcium chloride and potassium hydroxide, and a Hittorf tube. The apparatus was exhausted by means of a mercury pump, the flask being heated in a water-bath. With purple light in the Hittorf tube, most of the oil, evaporating from the surface without visible boiling, passed over at 73·5—74·5°, and was collected separately. The distillate was a highly refracting, colourless oil having D_{15}^{15} 1·1892. Analysis gave results showing close agreement with the formula C_4H_5ONS.

On keeping, especially in the light, the oil gradually became yellow, and finally dark-coloured.

Action of Hydrochloric Acid on Thiocyanoacetone.

It has already been shown that dilute aqueous hydrochloric acid does not produce any great alteration in thiocyanoacetone (Tcherniac, *Ber.*, 1892, **25**, 2618).

When 5 per cent. of its weight of hydrogen chloride is led into thiocyanoacetone, kept cool, a crystalline magma is formed which liquefies on keeping. On extraction with ether, the thiocyanoacetone is recovered apparently unaltered. A quite different result is obtained when the substance is saturated with hydrogen chloride.

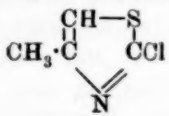
Thiocyanoacetone (115 grams: 1 mol.) was saturated with hydrogen chloride (70 grams), the whole being cooled with running water. After the resulting magma had completely liquefied, the syrup was dissolved in 500 c.c. of water, and the solution extracted with ether. The latter left on distillation 70 grams of a pale brown oil, which was distilled under 14 mm. pressure from a water-bath, and gave 40 grams of a colourless distillate passing over at 69°.

In another preparation the solution was distilled in a current of steam instead of being extracted with ether, and gave half the weight of the thiocyanoacetone taken.

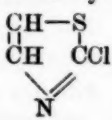
The oil was washed with dilute sodium hydroxide solution, dried over calcium chloride, and distilled. By far the greater part passed over at 167—167·5°/754·4 mm.

Found: C = 35·99; H = 3·2; N = 10·22; Cl = 26·43. S = 24·38.
C_4H_4NClS requires C = 35·95; H = 2·99; N = 10·48; Cl = 26·59; S = 23·97 per cent.

Apparently this substance is 2-chloro-4-methylthiazole (I), a



(I.)



(II.)

homologue of 2-chlorothiazole (II) (Schatzmann, *Annalen*, 1891, **261**, 10), the boiling point of which is 144—144·5°.

2-Chloro-4-methylthiazole is a colourless oil boiling at 167—167·5°/754·4 mm. and 69°/14 mm.; it has D_{15}^{15} 1·2992. It possesses a characteristic odour resembling that of pyridine, and slightly alkaline properties; thus, it dissolves in concentrated hydrochloric acid, but not in the dilute acid. It is comparatively stable; after boiling for twelve hours with a methyl-alcoholic solution of sodium methoxide, only one-twentieth of its chlorine was removed, and the bulk of the oil remained unaltered. In this respect it differs from chlorothiazole, which is said to retain the chlorine very loosely. This is not an isolated fact. The chemical behaviour of the members of the thiazole group is often so radically different from that of their methylated homologues (see Schatzmann, *loc. cit.*) that serious doubts must arise as to their analogy of structure.

It was found that of the 70 grams of hydrogen chloride absorbed by the thiocyanoacetone, 14 grams had been consumed in the reaction

$$C_4H_5ONS + HCl = C_4H_4NClS + H_2O.$$

The residue from the distillation of the ethereal extract, together with the aqueous solution from which the oil had been extracted, after neutralisation with sodium carbonate and further extraction with ether, yielded 25 grams of "hydroxymethylthiazole" (after purification by crystallisation).

The action of alcoholic hydrogen chloride on thiocyanoacetone will be described later.

Thiocyanoacetone and Ammonia.

The so-called hydroxymethylthiazole, which was obtained accidentally by Hantzsch and Weber (*Ber.*, 1887, **20**, 3127) in an attempt to prepare thiocyanoacetone, owed its formation to the circumstance that they had used sodium carbonate for salting out the thiocyanoacetone. As has been shown (*Ber.*, 1892, **25**, 2619), all alkaline substances possess the power of converting thiocyanoacetone into its isomeride. Aqueous ammonia produces exactly the same result. Hantzsch's statement (*Annalen*, 1888, **249**, 7) that the chief product of the action of ammonia on thiocyanoacetone is aminomethylthiazole (thiocyanopropimine) is devoid of all foundation, as may be seen from the following experiments.

Thiocyanoacetone (115 grams:1 mol.) was dissolved in 1500 grams of water, the solution cooled, and 50 c.c. of 20 per cent.

ammonia were added. Heat was evolved, and a yellow resin separated. After forty hours, the solution was filtered, and to the filtrate 172 c.c. of 25 per cent. hydrochloric acid were added, much carbon dioxide being evolved.

The acid solution was extracted with ether in the author's automatic apparatus (this vol., p. 1090), and the ethereal extract evaporated in the water-bath. The brown, syrupy residue was heated in a vacuum on the water-bath, when some water possessing the pungent odour of thiocyanic acid distilled over. The distillate gave the thiocyanate reaction and gradually deposited a small quantity of radially grouped yellow needles, which became dark at about 150° and decomposed at about 200° (perthiocyanogen?).

The residue from the distillation (63·5 grams) was boiled for some time with ether under a reflux condenser. After repeated crystallisations, about 25 grams of pure "hydroxymethylthiazole" were obtained from the solution, together with a small quantity of the yellow substance above-mentioned.

If any aminomethylthiazole had been formed, it must have remained in the hydrochloric acid solution which had been extracted with ether. This solution was therefore rendered alkaline with sodium hydroxide and completely extracted in the apparatus. The ethereal extract left on distillation 1·732 grams of a dark syrup only partly soluble in hydrochloric acid. The hydrochloric acid solution was filtered, warmed with animal charcoal to 50°, and again filtered. After several days, a black mud was deposited, which was filtered off. The filtrate was warmed with charcoal (0·5 gram) and again filtered. To the filtrate, hydrochloric acid was added, together with platinic chloride in excess, and the whole left to remain overnight, when the yellow precipitate was collected. When dry, it weighed 1·040 grams, proved insoluble in water or alcohol, and melted at about 220°. (Found: Pt = 30·36. $(C_4H_6N_2S,HCl)_2PtCl_4$ requires Pt = 30·34 per cent.)

Assuming this to be pure double salt, it corresponds with 0·477 gram of aminomethylthiazole from 115 grams of thiocyanoacetone. Moreover, as thiocyanate is formed in the reaction, there is no reason to think that even this minute quantity of the base owes its origin to anything more than the well-known action of ammonium thiocyanate on thiocyanoacetone (Norton and Tcherniac, *Ber.*, 1883, **16**, 345).

In view of the foregoing results, Hantzsch's explanation (*loc. cit.*, p. 26; compare Beilstein, "Handbuch der organischen Chemie," IV, 518) of the formation of aminomethylthiazole (thiocyanopropimine), namely, that by the action of ammonium thiocyanate on chloroacetone, thiocyanoacetone is first formed, and is

then converted by combination with free (!) ammonia into amino-methylthiazole, must be regarded as invalid.

The Isomerides of Thiocyanoacetone: Hydroxymethylthiazole, or α-Methylrhodim.

For reasons to be stated later, the so-called hydroxymethylthiazole will henceforth be known as α-methylrhodim.

The author has shown (*Ber.*, 1892, **25**, 3648) how α-methylrhodim is best prepared from thiocyanoacetone. The same method may be used for its preparation direct from chloroacetone.

To 92·5 grams of monochloroacetone, 1500 grams of water, 125 grams of potassium thiocyanate (or the equivalent amount of the sodium salt), and 30 grams of sodium hydrogen carbonate are added. The mixture is shaken from time to time and allowed to remain for ten days. A brown resin is gradually deposited, and the aqueous solution is filtered off and warmed to 45°. Twenty grams of animal charcoal are then added, and the mixture is left to remain for two hours and shaken from time to time. It is then filtered, and the filtrate extracted with ether in the apparatus. On an average, there accumulated in the flask containing the ether 33 grams of white needles, which, after being washed with ether, melted at 102—103°. From the ethereal solution, a further 14 grams were obtained, making in all 47 grams, that is, approximately 41 per cent. of the theoretical yield.

Instead of extracting with ether, a tedious operation in the absence of an automatically working apparatus, the aqueous solution can be evaporated in a vacuum from a water-bath, care being taken to keep the temperature of the bath below 60° until there remain about five parts of water for one of α-methylrhodim. On cooling, 75—80 per cent. of the substance will crystallise out, and the mother liquor may be further concentrated.

When less water or sodium hydrogen carbonate is used in the preparation, the yield is smaller.

Impure α-methylrhodim is best purified by recrystallisation from five times its weight of water at 55—60°. Thus, 41 grams of the crude product were dissolved in 205 grams of water, the solution being shaken with charcoal and filtered warm. The first crop yielded 32 grams of needles melting at 102—103°.

By utilising the mode of formation from ammonium thiocarbamate (observed by Marchesini, *Gazzetta*, 1893, **23**, ii, 442), the preparation of α-methylrhodim can be much more satisfactorily accomplished than by the above method. The way there followed, namely, heating in an alcoholic solution, is unsuitable as a method

of preparation. It required thorough modification to obtain from it a simple and practical method.

Ammonium thiocarbamate, $NH_2 \cdot CO \cdot S \cdot NH_4$, is easily obtained pure by leading carbonyl sulphide into alcoholic ammonia cooled with ice. The gas is readily absorbed, and a white, crystalline powder is soon deposited, which is rapidly collected, washed with alcohol, and dried in a vacuum over sulphuric acid. Two hundred and fifty c.c. of 4·14 per cent. alcoholic ammonia yielded 18·82 grams of the dry salt.

The thiocarbamate (14·3 grams: about 0·15 mol.) was dissolved in a little water, ice added, and 12 c.c. of monochloroacetone (13·95 grams = 0·15 mol.) were mixed with the solution, and the flask was imbedded in ice. Soon a violent reaction took place, when the chloroacetone dissolved, the ice melting within the flask. The slightly yellow liquid was filtered, and the filtrate (74 grams) left to remain overnight. It set to a paste of yellowish needles (12·85 grams, dry) melting at 101—102°. From the filtrate 3·2 grams were obtained, the total of more than 16 grams representing a yield of 93 per cent. The product was easily purified by one crystallisation from water.

This result, compared with the complications attending the preparation from thiocyanoacetone, renders highly improbable the intermediate phase

$$CH_3 \cdot CO \cdot CH_2 \cdot SCN + H_2O = CH_3 \cdot CO \cdot CH_2 \cdot S \cdot CO \cdot NH_2,$$

suggested by Hantzsch and Weber (*Ber.*, 1887, **20**, 3128) as part of the mechanism of the isomerisation.

α-Methylrhodim and Methyl Sulphate: Dimethylrhodim.

α-Methylrhodim (115 grams: 1 mol.) was dissolved in 500 c.c. of 2*N*-sodium hydroxide, and 95 c.c. of methyl sulphate (1 mol.) were gradually added, cooling with water. The solution was extracted with ether in the apparatus. The ether left 122·6 grams of a yellow oil, which solidified on cooling. When dissolved in its own volume of water, it showed a lower critical solution temperature. The slightest warmth, even that of the hand, induced separation into two layers, which mixed again on cooling. The solution was shaken with 10 grams of charcoal, filtered, the turbid filtrate concentrated in a vacuum at 35°, when it became clear again, and the concentration continued until the solution in the distillation flask weighed 145 grams. (A small quantity of oil distilled over with the water.) To the cold solution a tiny crystal from a previous preparation was added, and the whole left over sulphuric acid in a vacuum. Large crystals were gradually formed and removed

from time to time. In all, 65 grams were collected and recrystallised from a small quantity of water.

In another preparation, the crude product remaining after the distillation of the ether was drained on the vacuum pump from the oil which it contained, and was then washed with ether.

A quantity of crude product (20 grams) which had been kept for two years and had become brown and viscid was purified in the following manner. It was dissolved in water with the addition of 20 c.c. of *N*-sodium hydroxide and extracted with ether. The extract was almost colourless, and the aqueous solution yellowish-brown. The ether was evaporated, and left 17·322 grams of oil which soon solidified, the temperature rising to 46°. The substance was dissolved in its own weight of water at 25°, and when the solution assumed the ordinary temperature (17°), a fragment of a crystal was added. Overnight, large crystals separated (10·359 grams, m. p. 48—49°), and from the mother liquor a further crop was obtained (5·4 grams).

The original yellowish-brown solution which had been extracted with ether was acidified with hydrochloric acid and again extracted. The ether left 1·442 grams of a yellowish-brown oil which did not crystallise.

It appears from the foregoing that it will simplify the purification to add sodium hydroxide to the aqueous solution containing the product of the interaction of the sodium salt of α-methylrhodim and methyl sulphate before extracting with ether.

The substance after repeated crystallisations reached a maximum melting point, and was then analysed.

Found: C=46·22; H=5·81; N=10·52; S=25·20.
C_5H_7ONS requires C=46·51; H=5·43; N=10·85; S=24·80 per cent.

The substance is therefore dimethylrhodim,

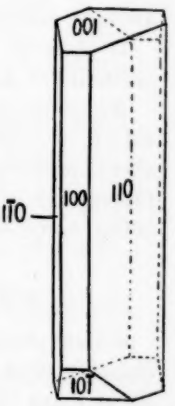
$$CH_3{\cdot}C_4H_4ONS.$$

It is very readily soluble in water or ether, and crystallises from the former in large, transparent prisms or plates melting at 49—50°.

The strong tendency of this substance to form large, well-defined crystals created a desire for the determination of its crystallographic characteristics.

This work has been kindly undertaken for me by Mr. G. M. Bennett, to whom I tender my warmest thanks. His report is as follows:

"Crystallographic examination of dimethylrhodim. Crystal system: monoclinic; holohedral class. Habit:



R R*

prismatic, with elongation parallel to the *c*-axis. Axial angle = 98°11′. Axial ratios: $a:b:c = 2{\cdot}580:1:1{\cdot}874$. Forms observed: (100), (110), (001), ($10\bar{1}$). There is a well-marked cleavage in the plane (100).

"The following are the regular measurements:

	Observed.	Calculated.
100–110	68°37′	—
110–$\bar{1}$10	42 51	42°46′
100–001	81 49	—
001–$\bar{1}$01	38 40	38 43
100–10$\bar{1}$	59 28	—
001–110	86 58	87 1
$\bar{1}$01–$\bar{1}$10	79 11	79 20

"The faces of the crystals were rather dull through abrasion, particularly the small ones, so that some of the values are a little uncertain."

Hydrolysis of Dimethylrhodim.

The substance (2·58 grams) was heated with 10 c.c. of hydrochloric acid (D 1·19) for two hours at 140° in a sealed tube. There was considerable pressure on opening the tube, and the escaping gas had an odour of hydrogen sulphide and mercaptan. The contents of the tube were washed out with water and distilled, when some oil, apparently chloromethylthiazole, passed over with the water. The residual liquid was rendered alkaline and distilled into hydrochloric acid so long as the evolved vapours gave an alkaline reaction.

Part of the hydrochloride was obtained as such. After crystallisation, it gave Cl = 52·26, whilst $CH_3{\cdot}NH_2{,}HCl$ requires Cl = 52·29 per cent. The remainder was converted into the platinichloride, which contained Pt = 41·12, whilst $(CH_3{\cdot}NH_2{,}HCl)_2PtCl_4$ requires Pt = 41·32 per cent.

No other base than methylamine was observed, and the total amount represented more than 90 per cent. of the theoretical.

It appears, therefore, that the methyl group introduced into the molecule of α-methylrhodim is attached to the nitrogen atom.

An attempt to prepare an *O*-ether from α-methylrhodim by the action of methyl iodide on the silver salt was unsuccessful. The alkaline solution is, indeed, precipitated by silver nitrate, but the precipitate consists chiefly of silver sulphide, part of the substance being destroyed.

α-Methylrhodim and Phosphorus Pentachloride.

α-Methylrhodim, which can be crystallised from warm phosphoryl chloride without any alteration, was dissolved in that solvent, a little more than the equivalent quantity (1 mol.) of phosphorus

pentachloride added, and the mixture heated to 50°. Hydrogen chloride was evolved, and a product was formed which was purified by repeated crystallisation from benzene.

Found: S=21·74.

C_4H_4ONClS requires S=21·40 per cent.

The chloride consists of pale brown, radially grouped acicular crystals melting and decomposing at 144°. It dissolves in dilute sodium hydroxide solution with a slight evolution of heat and the loss of the whole of its chlorine. On saturating the alkaline solution with carbon dioxide, a fine mud is deposited, which shrinks on drying to brown, brittle nodules (about 70 per cent. of the weight of the chloride) not melting at 220°.

The constitution of this product will be considered later.

Thiocyanoacetone and Alcoholic Hydrogen Chloride: β-Methylrhodim.

Hydrogen chloride (75 grams) was led into a mixture of thiocyanoacetone (115 grams: 1 mol.), alcohol (115 grams), and water (18 grams). On the following day, the mixture was placed in a vacuum over sulphuric acid and sodium hydroxide, and allowed to remain for several days. The brown residue (162 grams), containing a few crystals, was removed with water and extracted in the automatic apparatus. After some time, crystals began to appear both in the flask of boiling ether and in that of the aqueous solution. The extraction was continued for eight days until the crystals in the latter had disappeared. By that time, an abundance of crystals had accumulated in the ether flask, along with some brown oil. The latter was decanted with the ether, and the crystals were washed with ether and alcohol. The crystals (38 grams, dry) were dissolved under a reflux condenser in 760 grams of boiling water, charcoal was added, and the solution filtered hot. On cooling, white crystals were gradually deposited (33 grams).*

The same substance was formed when α-methylrhodim was left to remain for a long time in contact with concentrated hydrochloric acid, preferably in the presence of alcohol. A mixture of 11·5 grams of α-methylrhodim, 50 grams of hydrochloric acid (D 1·19), and 25 c.c. of alcohol yielded more than 3 grams of the substance.

Found: C=41·41; H=4·54; N=11·93; S=28·11.

C_4H_5ONS requires C=41·74; H=4·35; N=12·17; S=27·83 per cent.

* From the mother liquors chloromethylthiazole (18 grams) and α-methylrhodim (25 grams after purification) were obtained.

The substance, another isomeride of thiocyanoacetone, is named β-methylrhodim.

β-Methylrhodim is deposited from hot water as a white, crystalline powder; from alcohol by slow crystallisation in stout, colourless, quadratic plates melting at 183—184°. It dissolves in about 20 parts of boiling water and in about 475 parts at 15°. It is fairly readily soluble in boiling alcohol, less so in cold, and sparingly so in ether. When submitted to prolonged extraction in the apparatus with a relatively small quantity of ether, it accumulates in the boiling solvent and separates gradually in fine, colourless, transparent plates.

It is readily soluble in alkalis, and is precipitated therefrom by acetic acid.

β-Methylrhodim and Hydrochloric Acid.

β-Methylrhodim (3·45 grams) was heated with 30 c.c. of hydrochloric acid (D 1·19) for two hours at 100° in a sealed tube. There was no pressure on opening the tube, and the yellow solution yielded 3 grams of α-methylrhodim, together with a minute quantity (0·045 gram) of white crystals, which separated from the ethereal extract. They shrank, became brown at 250°, and did not melt at 265°. Whilst, therefore, β-methylrhodim is formed from α-rhodim under the influence of cold hydrochloric acid, the inverse conversion takes place almost completely at a higher temperature.

Thiocyanoacetone and Sodium Hydrogen Sulphite: iso*Methylrhodim.*

After prolonged heating of thiocyanoacetone on the water-bath, it was found to contain a crystalline substance, different from the then known derivatives. The same substance was obtained by the action of alkali hydrogen sulphites on thiocyanoacetone, and, after many attempts, a method was perfected which allowed it to be prepared with certainty and in a state of purity.

The action of free sulphur dioxide may be described first.

A solution of thiocyanoacetone (11·5 grams) in 150 grams of water absorbed 37 grams of sulphur dioxide, of which 26 grams were lost when the solution was left in a vacuum at the ordinary temperature. The solution was then extracted with ether, and yielded only 0·45 gram of a yellow oil. The extracted solution was concentrated to 20 c.c. in a vacuum on a water-bath at 40°. The residue, which still had the odour of sulphur dioxide, was again treated with ether, and yielded 8·24 grams of fairly pure thiocyanoacetone.

It would appear, therefore, that a sulphonic acid possessing a certain degree of stability is formed.

Quite different is the behaviour of thiocyanoacetone towards alkali hydrogen sulphites when they contain no free sulphur dioxide.

Thiocyanoacetone (230 grams : 2 mols.) was added to a mixture of 2150 c.c. of water and 360 c.c. of a 27·8 per cent. solution of sodium hydrogen sulphite, which was neutral towards methyl-orange. The temperature rose 11°. The solution was shaken with charcoal and filtered rapidly through a folded filter. After two days there was an abundant crystallisation. The crystals were collected (72 grams, dry) and recrystallised (66·5 grams, dry) from 1450 grams of boiling alcohol.

Found: C = 41·70; H = 4·29; N = 12·05; S = 27·66.

C_4H_5ONS requires C = 41·74; H = 4·35; N = 12·17; S = 27·83 per cent.

The substance has therefore the composition of thiocyanoacetone, and is a third isomeride of that compound; it will be named *iso*methylrhodim.

iso*Methylrhodim* is remarkable for its great power of crystallisation and sparing solubility in cold water or alcohol. It requires 16 parts of boiling and 400 parts of cold alcohol. It crystallises from alcohol in white, long, brilliant, interwoven needles melting at 127—128°.

It dissolves slowly in dilute sodium hydroxide solution, but with decomposition. When the orange-coloured solution is treated with carbon dioxide, it evolves hydrogen sulphide and deposits after a time a sparingly soluble salt (sodium cyanurate?).

The sodium hydrogen sulphite used for the preparation of *iso*methylrhodim does not act solely as a catalyst. Part of the aqueous mother liquor from which the *iso*methylrhodim had been separated, and containing a trace only of sulphuric acid, was distilled with hydrochloric acid, and the distillate collected in a receiver containing water and sodium hydrogen carbonate. A portion of the distillate was oxidised with bromine, and the sulphuric acid produced was estimated gravimetrically. The result revealed the consumption of 56·13 grams of sodium hydrogen sulphite, a little more than one molecule for four molecules of thiocyanoacetone.

Preparation of iso*Methylrhodim from Chloroacetone.*

Monochloroacetone (92·5 grams : 1 mol.) was stirred for two and a-half hours with 190 c.c. of a 47 per cent. solution of sodium

thiocyanate, cooling with water, when sodium chloride began to be deposited. A solution of 60 grams of crystallised potassium hydrogen sulphite in 300 c.c. of water was added, when nearly all dissolved, and the stirring was continued for half an hour. After two days, the yellow needles (44·27 grams, dry, m. p. 124—125°), containing some oil, were separated and recrystallised twice from 700 and 500 grams, respectively, of boiling alcohol, yielding, finally, 34·285 grams of white needles melting at 127—128°.

When sodium hydrogen sulphite solution was used instead of the crystallised potassium salt, the yield was much lower.

The various quantities of oil obtained in the different preparations were found to consist chiefly of thiocyanoacetone.

*iso*Methylrhodim and Hydrochloric Acid: Dithiazylamine.

Concentrated hydrochloric acid acts slowly on *iso*methylrhodim at the ordinary temperature, but rapidly on heating. *iso*Methylrhodim (23 grams) was boiled with 200 c.c. of concentrated hydrochloric acid and 66 c.c. of water under reflux for twenty minutes, when some hydrogen chloride was evolved. About half the liquid was then distilled off, a yellow oil passing over with the distillate. From the latter, ether extracted 1·5 grams of oil.

To the orange residue in the distillation flask, 300 grams of water were added, the whole was boiled for some time, filtered from a yellow resin, the solution treated with charcoal, and filtered hot. On cooling, faint yellow, efflorescent needles were deposited (10·2 grams, anhydrous), which were dissolved in 115 c.c. of boiling 8 per cent. hydrochloric acid, the solution being shaken with charcoal and filtered hot. On cooling, long, yellow, prismatic needles separated, which were collected and washed with the same dilute acid. After being pressed between filter paper, they weighed 13·1 grams; they contained water of crystallisation, as well as some hygroscopic moisture. In a vacuum over sulphuric acid and sodium hydroxide, they effloresced to a powder and lost about 27 per cent. of their original weight. For analysis, some of the substance was recrystallised as above.

Found: C = 39·09; H = 4·53; N = 16·69; Cl = 14·57; S = 26·09.
$C_8H_9N_3S_2,HCl$ requires C = 38·79; H = 4·04; N = 16·97; Cl = 14·34; S = 25·86 per cent.

Found: H_2O = 27·00.
$C_8H_9N_3S_2,HCl,5H_2O$ requires H_2O = 26·67 per cent.

The substance is a hydrochloride, the acid of which can be estimated by titration.

The compound crystallises in pale yellow needles which easily

lose their water of crystallisation, crumbling to a fine, yellow powder which does not melt at 250°, but appears to sublime and decompose.

One part of the anhydrous salt is soluble in 46·25 parts of water at 26° and in 3—4 parts of hot water. The hydrate is fairly soluble in concentrated and sparingly so in dilute hydrochloric acid. The latter is a very convenient solvent for its purification; thus, one part of the hydrate (equal to 0·733 part of the anhydrous salt) dissolves in about 9 parts of hot 10 per cent. hydrochloric acid, whilst it requires more than 130 parts of the cold acid of the same strength. It separates from alcohol as a yellow, crystalline powder.

The Base, $C_8H_9N_3S_2$.

The aqueous solution of the hydrochloride is precipitated by alkali hydroxides, when these are not in excess, or by alkali carbonates.

The hydrochloride (57 grams) was dissolved in 2600 grams of water, the slightly turbid solution filtered, 115 c.c. of 2*N*-sodium hydroxide were added to the filtrate, and the white, voluminous, caseous precipitate was collected (48 grams, dry, instead of the theoretical 48·6 grams, m. p. 148—150°).

The 48 grams were recrystallised from 340 grams of hot alcohol. On cooling, yellowish, asbestos-like needles were deposited (38·4 grams, dry, m. p. 150—151°). The mother liquor yielded a further quantity (8·8 grams).

For analysis, the substance was twice recrystallised from a mixture of benzene and light petroleum.

Found: C = 45·37; H = 4·57; N = 19·69, 19·74.

$C_8H_9N_3S_2$ requires C = 45·49; H = 4·27; N = 19·90 per cent.

The base crystallises from the above solvent in almost white, spherical clusters of needles; from alcohol, in felt-like aggregates of long, silky needles melting at 153—154°. It dissolves in about 5 parts of hot and 37 parts of cold alcohol. It is insoluble in water or alkali carbonates, but soluble in alkali hydroxides.

Determination of Molecular Weight by the Cryoscopic Method.

Weight of solute. Gram.	Weight of of solvent. Grams.	Nature of solvent.	Δ.	M.W.
0·1077	12·945	Benzene	0·13°	313·6
0·1659	,,	,,	0·20	313·8
0·1107	19·630	Nitrobenzene	0·105	351·6
0·1674	,,	,,	0·172	357·5
			Average	334·0

$C_8H_9N_3S_2$ requires M.W. = 211.

Determination of Molecular Weight by the Ebullioscopic Method.

0·1939 Gram of substance in alcohol. Constant for 100 c.c. = 15·6.

Rise in temperature.	Grams in 100 c.c.	M.W.
0·110°	2·938	416·7 (?)
0·137	2·620	298·3
0·120	2·365	307·4
0·107	2·154	314·0
	Average	334·0

The average happens to be the same by both methods, but the individual results are too divergent to make the average appear conclusive; it corresponds approximately with 1·5 times the simple formula $C_8H_9N_3S_2$. Since this formula cannot be multiplied by 1·5, the only recourse is to double it, unless, indeed, we admit molecular aggregation in solution, a phenomenon which does not appear uncommon in the case of complicated compounds.

A determination by Zerewitinov's method (*Ber.*, 1907, **40**, 2023; 1908, **41**, 2233) of the active hydrogen in the base, in pyridine solution, cold or hot, gave respectively 1·274 and 1·476 atoms of hydrogen per molecule of the formula $C_8H_9N_3S_2$. Of course, it is not impossible that the substance undergoes a far-reaching change under the influence of magnesium methyl iodide.

As will be seen later, when the structure of the group C_4H_4NS is discussed, the base is probably *dithiazylamine*, $(C_4H_4NS)_2NH$.

Examination of the Oil.

The oil, the second product of the action of hydrochloric acid on *iso*methylrhodim, was distilled under 14 mm. pressure several times, when it passed over at 94—97° (mostly at 96—97°), each time leaving a residue and undergoing slight decomposition. It would no doubt distil unchanged under still lower pressure.

As was to be expected, the results of the analysis were only approximate.

Found: C = 49·14; H = 5·67; S = 45·24.

C_3H_4S requires C = 50·00; H = 5·55; S = 44·44 per cent.

Determination of Molecular Weight by the Cryoscopic Method. In Glacial Acetic Acid.

Weight of solute. Gram.	Weight of solvent. Grams.	Δ.	M.W.
0·1530	20·91	0·205°	139·2
0·3792	,,	0·515	136·3
0·5322		0·720°	137·8

$C_6H_6S_2$ requires M.W. = 144.

The formula, C_3H_4S, has therefore to be doubled. A determination by the ebullioscopic method gave the number 188.

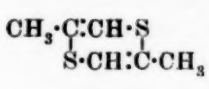
The compound is a colourless, highly refractive oil having a characteristic odour reminiscent of turpentine. It dissolves in concentrated sulphuric acid, yielding an orange-coloured solution which is not precipitated by water.

The formation of this substance, jointly with that of the base, may be accounted for as follows:

$$6C_4H_5ONS = 2C_8H_9N_3S_2 + C_6H_8S_2 + 2CO_2 + 2H_2O.$$

About two-thirds of the quantity of the base to be expected from this equation is obtained and one-third of the amount indicated for the compound, $C_6H_8S_2$.

The structural formula of $C_6H_8S_2$ may be represented by I, and



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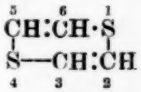


(II.)

if the ring (II) be termed thiën, the compound, $C_6H_8S_2$, will be 2:5-*dimethylthiën*.

iso*Methylrhodim and Methyl Iodide.*

Five sealed tubes each containing 7 grams of *iso*methylrhodim, 10 grams of methyl iodide, and 20 grams of methyl alcohol were heated for three hours at 125°. On opening the tubes, the escaping gas had a fishy odour and contained carbon dioxide. The brown liquid, containing needle-shaped crystals, was removed with methyl alcohol and distilled from a water-bath. The residue (53·75 grams) was boiled with 750 c.c. of water, the solution filtered from a black tar, and boiled with charcoal. On cooling, a mixture (3·835 grams) of compact crystals (*A*) and of fine needles was deposited and separated mechanically; the latter proved to be unaltered *iso*methylrhodim.

The mother liquor was reduced by distillation to about 250 c.c. Along with the water, a small quantity of a malodorous oil and some solid matter passed over, which gave an ethereal extract of 0·622 gram.

The aqueous residue from the distillation was boiled with animal charcoal and filtered hot. On cooling, crystals (1·4 grams) similar to (*A*) were deposited.

The filtrate was now concentrated to 50 c.c., and yielded a further quantity (2·67 grams) of the same substance. The final mother liquor (*B*) will be mentioned later.

The three crystallisations of (*A*), together weighing about 7 grams, were dissolved in 400 grams of boiling water, the solution treated with charcoal, and filtered hot. The crystalline deposit (4·405 grams, dry) was recrystallised from 135 grams of water, and yielded 3·467 grams of long, colourless, massive crystals not melting at 265°. When heated on platinum, they sublimed without melting (Found: C = 27·80; H = 2·53; N = 33·09. CHON requires C = 27·90; H = 2·33; N = 32·72 per cent.).

The substance has therefore the composition of cyanuric acid, the properties of which it possesses. Thus, it gives Hofmann's reaction with sodium hydroxide and Wöhler's with copper sulphate.

The final mother liquor (*B*) was distilled in a vacuum to dryness, and the residue (23·51 grams) crystallised from alcohol. White plates (13·07 grams) were obtained which volatilised completely at about 220° with the evolution of iodine (Found: C = 18·15; H = 4·54; S = 15·47; I = 61·54, 62·13. C_3H_9Si requires C = 17·65; H = 4·41; S = 15·68; I = 62·25 per cent.).

The compound is therefore trimethylsulphine iodide.

It thus appears that under the influence of methyl iodide at a comparatively low temperature, *iso*methylrhodim undergoes complete disruption.

Comparative Examination of the Three Rhodims. Determination of Molecular Weight by the Cryoscopic Method.

α-Methylrhodim, m. p. 103—104°.

Weight of solute. Gram.	Weight of solvent. Grams.	Nature of solvent.	Δ.	M.W.	Average.
0·1342	21·385	Nitrobenzene	0·26°	173·8	—
0·0845	,,	,,	0·14	183·8	178·8
0·3380	27·925	Glacial acetic acid	0·405	114·1	—
0·3412	,,	,,	0·40	117·1	115·6

β-Methylrhodim, m. p. 183—184°.

0·094	22·005	Glacial acetic acid	0·110°	151·4	—
0·1604	,,	,,	0·14	203·0	177·0

iso*Methylrhodim*, m. p. 127—128°.

0·1080	19·57	Nitrobenzene	0·105°	378·0	—
0·079	,,	,,	0·065	404·7	391·35

Determination of Molecular Weight by the Ebullioscopic Method.

In alcohol: constant for 100 c.c., 15·6.

Preliminary tests with acetanilide gave an average M.W. = 157 instead of 135.

α-Methylrhodim, m. p. 103—104°: 0·3312 gram.

Rise in temperature.	Grams in 100 c.c.	M.W.	Average.
0·620°	5·018	126·2	—
0·554	4·476	126·0	—
0·496	4·039	127·0	—
0·440	3·680	130·5	127·4

β-Methylrhodim, m. p. 183—184°: 0·2175 gram.

0·155°	3·295	331·6	—
0·137	2·939	334·7	—
0·125	2·652	331·0	—
0·110	2·417	342·7	336·66

iso*Methylrhodim*, m. p. 127—128°: 0·1732 gram.

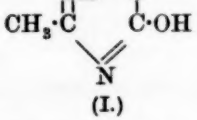
0·078°	2·624	524·8	—
0·070	2·340	522·0	—
0·060	2·112	549·1	—
0·052	1·924	577·2	543·1

C_4H_5ONS requires M.W. = 115.

Owing evidently to anomalies of aggregation, the results are not so conclusive as might be desired. α-Methylrhodim has certainly the simple molecule C_4H_5ONS, whereas there is some uncertainty concerning the two other isomerides. The author is inclined to regard β-methylrhodim as $2(C_4H_5ONS)$ and *iso*methylrhodim as $4(C_4H_5ONS)$, the structure of the ring, C_4H_5ONS, not being necessarily the same in the three isomerides.

Constitution of the Three Methylrhodims.

The so-called *meso*-hydroxymethylthiazole has, according to Hantzsch and Weber (*Ber.*, 1887, **20**, 3127), the structural formula I, which is that of a tertiary alcohol or phenol. The only fact



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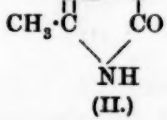
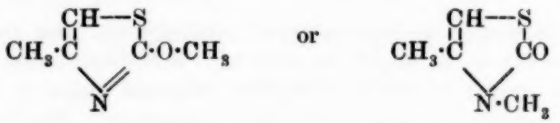


(II.)

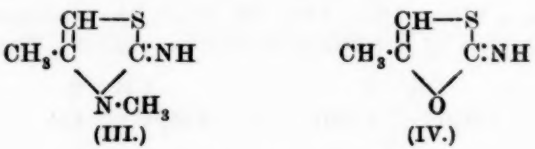
adduced by Hantzsch and Weber in favour of this formula was the alleged formation of *meso*-aminothiazoles by the action of ammonia

or primary bases. Later, however, Hantzsch had to admit the complete indifference of that compound towards ammonia or organic bases, having discovered that the reacting substance was thiocyanoacetone alone. This, and similar facts which were gradually evolved in the study of the aminothiazoles, led to these substances being represented as perfect models of tautomerism, hydroxymethylthiazole being endowed with a ketonic double (II), in spite of the absence of properties commonly possessed by ketones, as had been pointed out by Hantzsch and Weber themselves.

The author's long acquaintance with hydroxymethylthiazole has failed to reveal to him a single fact pointing to the presence of either a hydroxyl or a carbonyl group in that compound. It behaves neither as an alcohol nor as a ketone, and it affords no justification whatever for the assumption of tautomerism, that last resort of a formula in difficulties. Furthermore, the action of phosphorus pentachloride, which, as has been shown, leaves the oxygen intact, whilst it introduces chlorine into the molecule, makes the presence of either a hydroxyl or a carbonyl group at least improbable. The two formulæ (I and II) are, however, not only improbable, but impossible, as is proved by the study of the hydrolysis of the methylated derivative, $CH_3 \cdot C_4H_4ONS$, which the author has succeeded in obtaining in a state of purity. Indeed, this substance would have to be represented as



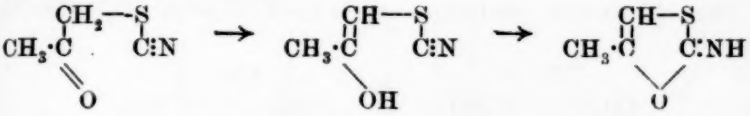
The first of these formulæ is that of an *O*-ether which can give no methylamine on hydrolysis; neither can a substance possessing the second formula, since the $N \cdot CH_3$ group is in the position 3, which, as Traumann (*Annalen*, 1888, **249**, 44) has shown in the case of 2-imino-3:4-dimethyl-2:3-dihydrothiazole (III), yields ammonia on hydrolysis, but no methylamine.



The compound, $CH_3 \cdot C_4H_4ONS$, on the contrary, gives a quantitative yield of methylamine.

We are thus led to the conclusion that the group $N \cdot CH_3$ occupies the position 2, which brings us to the formula IV for "hydroxy-

methylthiazole." A compound of this structure may be derived from thiocyanoacetone if it is assumed that the latter passes into the enolic form, that a hydrogen atom then migrates, and, finally, that the chain is closed,

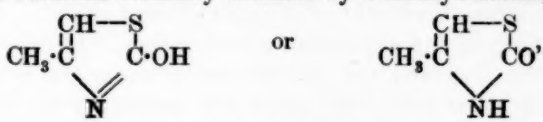


It appears, therefore, that the substance which has been known since 1887 as hydroxymethylthiazole is not a thiazole at all. It might be called 2-imino-4-methylthioxole, but for the sake of simplicity, and in view of the now proved existence of two other isomerides of thiocyanoacetone, it seems preferable to adopt the generic name *rhodim* for this class of compounds.

Thus, hydroxymethylthiazole becomes *α*-methylrhodim; the isomeride melting at 183—184°, *β*-methylrhodim; the isomeride melting at 127—128°, *iso*methylrhodim.

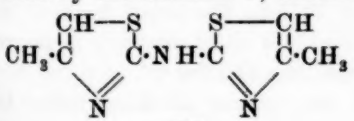
It has been shown that the first two can be easily converted into one another. They stand, therefore, in the closest connexion and have to be considered as structurally analogous, the only difference being in the size of the molecule, that of the *β*-isomeride being probably double.

The same cannot be said of *iso*methylrhodim; its chemical behaviour, which is quite different, goes to show that it possesses one of the formulæ formerly claimed by *α*-methylrhodim,

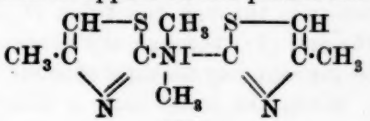


more likely the latter. A glance at it shows pre-existing the fragments, $CH_3{\cdot}C{:}CH{\cdot}S$, $\cdot CO{\cdot}NH\cdot$, etc., into which the compound can be made to decompose. The formula is, of course, not simple; it would have to be multiplied probably by 4, which could cause it to rank with cyanuric acid, the identity of which with tetracarbamide has been recently demonstrated (Walters and Wise, *J. Amer. Chem. Soc.*, 1917, **39**, 2472).

The base, dithiazylamine, $C_8H_9N_3S_2$, which is formed from *iso*methylrhodim by the action of hydrochloric acid, may be represented by the formula V, which makes it appear as the parent sub-



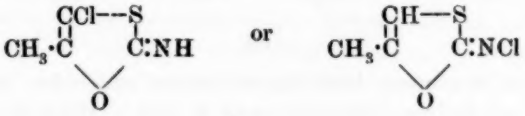
(V.)



(VI.)

stance of the ammonium hydriodide, $C_{10}H_{14}N_3IS_2$, obtained by Hantzsch and Weber (*Ber.*, 1887, **20**, 3131) in small quantity by the action of methyl iodide on aminomethylthiazole, to which, starting from another direction, they assigned the structural formula VI.

The chlorinated derivative of α-methylrhodim, C_4H_4ONClS, may be



more likely the first.

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XCIII.—*An Automatic Extraction Apparatus.*

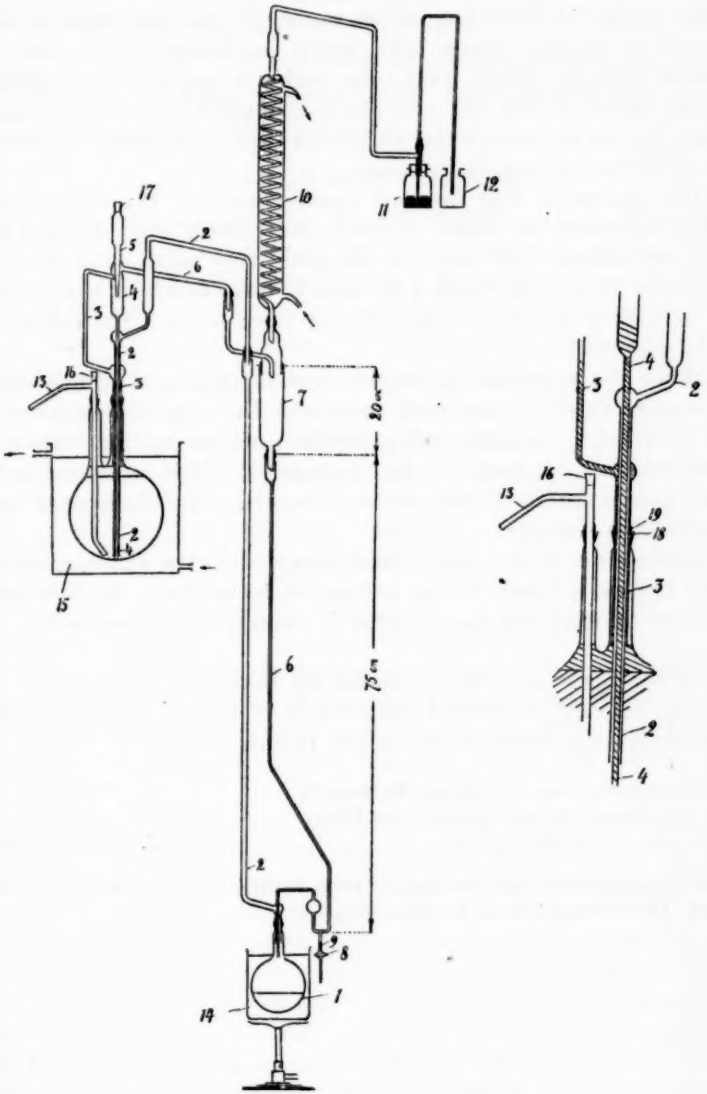
By JOSEPH TCHERNIAC.

THE extraction apparatus described by the author (*Ber.*, 1893, **25**, 3652), and frequently mentioned in the preceding paper, has undergone so many changes in the course of time that it seems desirable to give an account of it in its present shape.

The working of the apparatus is very simple. Of the two flasks shown in the diagram, the smaller one receives the ether and is heated in a water-bath; the large two-necked flask contains the solution to be extracted; it can be filled through the opening (16) of the tube (13), which is also used for siphoning off the exhausted liquor. The capacities of both flasks may vary within very wide limits, from a fraction of a litre to several litres. The two-necked flask is placed in a vessel through which cold water is run; it is then filled nearly to the neck with the liquid to be extracted, the tubes (16 and 13) are closed, and ether is poured in through the opening (17) of the tube (5). The ether flows through the tube (4) to the bottom of the flask, rises in the aqueous liquid and in the annular space between the tubes (3 and 2) (see enlarged inset), and descends through the tubes (6 and 7) into the small flask, filling the seal (9); through the condenser (10) a little mercury is poured to prevent any leakage of ether from the tap (8).

When the water-bath is heated, the vapour of ether raises the liquid ether in the seal to a certain height in the tube (6), and

also passes through the tube (2) to the bottom of the two-necked flask, where it is condensed; the liquid ether then returns through the tubes (3 and 6) and the seal into the small flask. Any aqueous



liquid carried over with the ether returns through the tube (4) into the two-necked flask.

By regulating the flow of water in the vessel (15), the tempera-

ture of the aqueous liquid can either be kept quite low or allowed to rise more or less.

The joints are very simple and efficient. As seen in the sketch (inset), the outer tube is very slightly conical (18), and the inner tube, which is little less in diameter, is provided with a short length of rubber tubing (19), which, on being pressed into the conical opening of the outer tube, makes a perfectly tight joint.

The mercury trap (11 and 12) is connected with the apparatus after the air has been expelled by the vapour of ether; it prevents losses of the solvent by diffusion.

The apparatus may be used equally well for the extraction of solid substances by means of ether, chloroform, etc. In this case, the two-necked flask may be comparatively small, and the tube (7) must be provided with a thimble or filter to arrest any particles of solid that may be carried over by the solvent. The cap of this tube is ground in.

When the apparatus is properly put together and in good order, it may be safely left to work overnight, the requisite condition for its satisfactory working being steady, uniform boiling with entire freedom from all tendency to "bumping." This is secured by the well-known device of introducing into the ether flask small tetrahedra of platinum.

Little ether is lost except that dissolved in the aqueous solution, and if care is taken before extraction to saturate the latter with sodium chloride, the loss of ether is rendered still smaller.*

In conclusion, I wish to express my thanks to my assistant, Mr. H. A. Steinmann, for the preparation of the excellent diagram of the apparatus which is the subject of this paper.

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49, PALACE ROAD, STREATHAM HILL,
LONDON, S.W. 2. [*Received, July 1st*, 1919.]

* The apparatus can be obtained from Messrs. Baird & Tatlock (London) Ltd., 14–15, Cross Street, London, E.C. 1.

XCIV.—*The Constitution of Carbamides. Part IX. The Interaction of Nitrous Acid and Mono-substituted Ureas. The Preparation of Diazomethane, Diazoethane, Diazo-n-butane, and Diazoisopentane from the Respective Nitrosoureas.*

By Emil Alphonse Werner.

Nitrosomethylurea, obtained by von Brüning (*Ber.*, 1888, **21**, 1809), was the first example of the preparation of a nitroso-derivative from a mono-substituted urea, and its formation has been supposed to take place in accordance with the equation

$$NH_2\cdot CO\cdot NH\cdot CH_3 + HNO_2 = NH_2\cdot CO\cdot N(NO)\cdot CH_3 + H_2O.$$

Later, nitrosophenylurea, and the corresponding *m*- and *p*-tolyl and β-naphthyl derivatives, were prepared by Walther and Wlodkowski (*J. pr. Chem.*, 1899, [ii], **59**, 285).

Assuming the carbamide configuration, it must be admitted that the formation of a nitroso-derivative is rather surprising and requires some explanation, since it would be natural to expect that the amino-group would be at once attacked with complete decomposition of the urea, thus:

(*a*) $NH_2\cdot CO\cdot NHR + HNO_2 = N_2 + CO_2 + NH_2R + H_2O.$

Moreover, the yield of nitroso-derivative was not sensibly affected by an addition of an excess of nitrous acid to the substituted urea, nor had nitrous acid any further action on the nitroso-compound when once formed. The latter, therefore, could not contain an amino-group.

A quantitative study of the changes involved has brought to light some interesting facts bearing on the question of the constitution of mono-substituted ureas, whilst the nitroso-derivatives examined are of more than ordinary interest, since they are likely to prove most useful substances for the simple preparation, and study, of the reactions of diazomethane and its homologues.

When methylurea in aqueous solution ($N/5$) was treated with nitrous acid in the presence of sulphuric acid, there was an immediate violent evolution of nitrogen and carbon dioxide, which ceased after a few seconds. This was quickly followed by the separation of crystals of a nitroso-derivative, the yield of which was, in round numbers, equal to 90 per cent. of the theoretical (Expts. 1 and 2).

In the case of ethyl-, *n*-butyl-, and *iso*amyl-urea, whilst similar

phenomena were observed, the yields of the respective nitroso-derivatives were approximately 76, 67, and 48 per cent. of the theoretical.

With benzylurea and phenylurea, respectively, where it was necessary to use a relatively large proportion of pure acetic acid to effect solution, 42 and 33 per cent. of the theoretical proportions of the nitroso-derivatives were formed.

The remainder of the respective ureas was decomposed according to equation (*a*), as proved by the evolution of larger volumes of carbon dioxide and nitrogen in proportion to the lower yields of nitroso-derivatives, and since the velocity of reaction (*a*) was greater than that which gave rise to the latter compounds, the evidence goes to show that the proportions of each substituted urea present in solution with a true "carbamidic" structure must be different.

In connexion with this point, it is important to note that the tendency to form a nitroso-derivative falls as the electropositive character of the hydrocarbon radicle diminishes. In the light of the facts just stated, this reaction is properly represented thus:

(*b*) $OH\cdot C(:NH)\cdot NHR + HO\cdot NO = OH\cdot C(:NH)\cdot N(NO)R + H_2O$.

An outstanding property of the aliphatic nitroso-derivatives is their immediate decomposition by alkalis, which in the case of the methyl derivative takes place quantitatively, as follows:

(*c*) $OH\cdot C(:NH)\cdot N(NO)\cdot CH_3 + NaOH = NaOCN + CH_2N_2 + 2H_2O$.

This change,* together with several other reactions described in the experimental part, supports the above constitution. It follows, therefore, that, so far as their behaviour towards nitrous acid is concerned, mono-substituted ureas in acid (sulphuric, hydrochloric, or nitric) solution are present in two forms in equilibrium, thus:

$$(A)\ NH_2\cdot CO\cdot NHR \rightleftharpoons OH\cdot C(:NH)\cdot NHR\ (B)$$

the proportion of each form being regulated by the electrochemical nature of the radicle (R).

Methylurea, for example, must be very largely presented for attack in the form (*B*), the formation of a salt of the type

$$OH\cdot C(:NH)\cdot NHR,HX$$

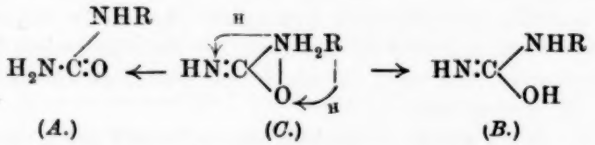
being promoted by the presence of the strongly electropositive methyl group. Phenylurea, on the other hand, is mainly present in the form (*A*), since the tendency to salt-formation is here distinctly feeble.

* The secondary reaction, resulting from the decomposition of diazomethane by water, is not considered here, and is dealt with later. In the case of the ethyl, *n*-butyl, and *iso*amyl compounds, some olefines are produced along with the diazo-derivative.

Further evidence in favour of the above view was found in the fact that mono-substituted ureas were directly attacked by nitrous acid in solution alone, even at a concentration of $N/18$, and whilst the velocity of the reaction at this low concentration was bound to be slow, it was quite appreciably promoted by the presence of a weak acid, such as acetic, particularly at concentration $N/5$ (Expt. 3).

In this respect, the substituted ureas differed markedly from urea itself (compare T., 1917, **111**, 864), and whilst the velocity of the reaction was slow, the end result was much the same as in the presence of a strong acid.

The probable existence of a cyclic form of the urea capable of giving rise to either forms (*A*) or (*B*) by migration of hydrogen, thus:



(*A.*) (*C.*) (*B.*)

must be taken into consideration as a likely condition in a neutral solvent or in the presence of a weak acid. The diminished velocity in the reaction with nitrous acid under such conditions becomes intelligible, since form (*C*), like urea itself, would not be attacked by the reagent. Whilst the behaviour of di- and tri-substituted ureas towards nitrous acid is under investigation, it may be mentioned here that nitrosodiethylurea, NHEt·CO·NEt·NO, readily furnished diazoethane on treatment with either sodium hydroxide or sodium ethoxide.

Experimental.

Interaction of Nitrous Acid and Methylurea. Preparation and Properties of Nitrosomethylurea.

All the gasometric experiments described were performed in a Lunge nitrometer, and, for the sake of brevity, only the volumes corrected to *N.T.P.* are given in each case.

Expt. 1.—0·074 Gram of methylurea and 0·072 * gram of sodium nitrite (equal molecular proportions) were dissolved in 3 c.c. of water, and 2 c.c. of *N*-sulphuric acid added. The concentration was $N/5$. After one minute, there was sudden separation of crystals (the nitroso-derivative), and the evolution of gas at once ceased.

* The equivalent of 0·069 gram of *pure* sodium nitrite.

Vol. of N_2=2·3 c.c.=10·26 per cent. of the theoretical for equation (*a*). Theory=22·4 c.c. N_2.

The gas was expelled from the nitrometer, and 2 c.c. of 15 per cent. potassium hydroxide solution were added to the residue. There was instant violent evolution of gas of a deep yellow colour (CH_2N_2), which gradually became colourless after remaining over the aqueous solution for some time.

Vol. of N_2=20·12 c.c.=89·82 per cent. of the theoretical for the formation of the nitroso-derivative according to equation (*b*). Theory=22·4 c.c. N_2.

Expt. 2.—0·074 Gram of methylurea and 0·144 gram of sodium nitrite were dissolved in 2 c.c. of water (HNO_2 to methylurea=2:1), and 3 c.c. of *N*-sulphuric acid added.

Vol. of N_2=2·4 c.c.=10·71 per cent. of the theoretical.

After addition of potassium hydroxide solution to the residue, vol. of N_2=19·95 c.c.=89·06 per cent. of the theoretical for the nitroso-derivative, the yield of which was therefore unaffected by an excess of nitrous acid.

Expt. 3.—0·074 Gram of methylurea and 0·072 gram of sodium nitrite were dissolved in 17 c.c. of water, and 1 c.c. of *N*-sulphuric acid was added. The concentration was *N*/18, and no free sulphuric acid was present. The evolution of gas was very slow, and at the end of twenty hours vol. of N_2=1·6 c.c.=7·14 per cent. of the theoretical.

Vol. of N_2=17·88 c.c. (after addition of potassium hydroxide)=79·82 per cent. of the nitroso-derivative formed.

Whilst the reaction in this case was not completed after twenty hours, the results prove that methylurea is directly attacked by nitrous acid alone on the same lines as in the presence of a strong acid. When an excess of acetic acid was present, the reaction was completed in about ten hours with results similar to those described in Expts. 1 and 2.

The following procedure was found most suitable for the preparation of nitrosomethylurea on a larger scale.

Methylurea (44·4 grams) and sodium nitrite (43·2 grams) were dissolved in 400 c.c. of water contained in a wide-mouthed bottle of 1200 c.c. capacity partly immersed in ice-cold water. A cold solution of 30 grams of pure sulphuric acid in 150 c.c. of water was gradually added, the liquid being well stirred. After two hours, the nitroso-derivative, which had separated, was collected, washed, and dried in a desiccator; it weighed 49·4 grams. The filtrate (and washings) was extracted twice with 80 c.c. of ether, from which solvent, after distillation at a gentle heat, 2·2 grams of the nitroso-compound were obtained. Total yield=51·6 grams, or

83·5 per cent. of the theoretical. On account of the vigorous evolution of gas and the simultaneous separation in microcrystalline form of the nitroso-compound, the latter was almost entirely carried to the surface as a thick froth; for this reason, the use of a flask should be avoided.

When sulphuric acid was replaced by about twice its equivalent of pure acetic acid in the above preparation, the nitroso-compound separated in highly refractive, tetragonal prisms, there was much less frothing, but it was necessary to allow the preparation to continue for not less than twenty-four hours before the maximum yield was attained, which even then was about 10 per cent. less than when sulphuric acid was used. Whilst individual crystals of nitrosomethylurea appear quite colourless, in bulk the compound has a pale buff colour rather than yellow, as described by von Brüning (*loc. cit.*). The crystals are readily soluble in alcohol, acetone, or ether, moderately so in benzene or chloroform, and almost insoluble in cold water.

On exposure to sunlight, the compound gradually loses its buff colour and becomes pale sea-green; beyond a fall in the melting point, this change had no apparent effect on the general reactions of the substance.

When an alcoholic solution of nitrosomethylurea was heated to the boiling point, it was gradually decomposed, thus:

$$OH\cdot C(:NH)\cdot N(NO)\cdot CH_3 \longrightarrow N_2 + CH_3\cdot OH + HNCO \rightleftharpoons HOCN.$$

Ethyl allophanate was produced as a result of the interaction of cyanic acid and ethyl alcohol.

In connexion with this decomposition, a curious difference was found in the stability of specimens of nitrosomethylurea prepared in the presence of sulphuric acid and of acetic acid respectively.

Expt. 4.—(*a*) A solution of 5 grams of nitrosomethylurea (acetic acid preparation) in 70 c.c. of alcohol was boiled under reflux; the buff-yellow colour of the solution gradually disappeared, and, after two hours, the solution was colourless. On cooling, ethyl allophanate, identified by its melting point (191°) and properties, separated, and the amount ultimately obtained was 2·28 grams, or 71·24 per cent. of the theoretical (theory = 3·2 grams from 5 grams of nitrosomethylurea). (*b*) A similar experiment with a specimen prepared in sulphuric acid solution gave, after two hours, 27·4 per cent., and after three hours only 40·94 per cent. of the theoretical yield of ethyl allophanate. For the present, no explanation can be offered for this apparent anomaly, which has been verified with several specimens.

Nitrosomethylurea melted at 121° (crystals from ether), and in

contrast to the foregoing change was violently decomposed, as follows:

(*d*) $OH\cdot C(:NH)\cdot N(NO)\cdot CH_3 = N_2 + CH_3\cdot NCO + H_2O$.

Most of the *iso*cyanic ester was obtained as the polymeride, $(CH_3\cdot NCO)_3$, which melted at 177° (Hofmann gives 176°).

Preparation of Diazomethane from Nitrosomethylurea.

In order to obtain the best yield of diazomethane in solution in ether, either of the following methods can be recommended.

Expt. 5.—Nitrosomethylurea (10·3 grams) in microcrystalline form was introduced into a round-bottomed flask of about 100 c.c. capacity, 50 c.c. of pure ether (distilled over sodium) were poured down the side of the flask, which stood in melting ice, and, without delay, 20 c.c. of 70 per cent. potassium hydroxide solution were quickly added drop by drop, while a quiet, circular motion was given to the flask. After about ten minutes, the deep golden-yellow, ethereal solution was decanted. It contained 3·2 grams of diazomethane, determined by the iodine method, which was equal to 76·2 per cent. of the theoretical for equation (*c*).

Whilst it was not possible to avoid decomposition of a considerable proportion of diazomethane by the water generated during the reaction, the effect was slightly reduced by altering the order of procedure; thus, when nitrosomethylurea was added in portions of about 0·5 gram at a time to very concentrated potassium hydroxide solution lying under the surface of ether, a solution of diazomethane was obtained which contained 78—79 per cent. of the theoretical.

In studying the use of diazomethane as a methylating agent, it has been apparently the universal practice to employ the substance exclusively in ethereal solution. This has obviously a serious disadvantage, on account of the limitations of ether as a solvent for many types of organic compounds. There seems no reason why this practice should be so rigidly adhered to, as shown by the following experiments.

Expt. 6.—To a solution of 1·03 grams of nitrosomethylurea in 40 c.c. of pure alcohol, a molecular proportion of sodium ethoxide in 10 c.c. of alcohol was added. Sodium cyanate was immediately precipitated, accompanied by a quiet evolution of nitrogen, which ceased at the end of about fifteen minutes, and a rich yellow solution of diazomethane was obtained. To 5 c.c. of the solution placed in the nitrometer, 10 c.c. of water were added; there was immediate brisk evolution of nitrogen, while the liquid became colourless.

Vol. of N_2 (measured over water) = 17·91 c.c. Hence for total

solution = 179·1 c.c. Theory = 224 c.c. Therefore the solution contained 79·9 per cent. of the theoretical proportion of diazomethane.

Expt. 7.—A solution of 0·103 gram of nitrosomethylurea in 3 c.c. of alcohol was introduced into the nitrometer, and 0·068 gram of sodium ethoxide in 2 c.c. of alcohol was added.

After twenty hours, only 4·5 c.c. of nitrogen (corrected for pressure of alcohol vapour) were evolved.

The gas was expelled from the nitrometer, and 10 c.c. of water were added, when there was immediate rapid evolution of nitrogen.

Vol. of N_2 = 16·84 c.c. (Theory = 22·4 c.c.)

The solution therefore contained, after remaining for twenty hours, 75·3 per cent. of the theoretical amount of diazomethane.

It will be seen from the equation,

$$OH\cdot C(:NH)\cdot N(NO)\cdot CH_3 + C_2H_5\cdot ONa = NaOCN + CH_2N_2 + H_2O + C_2H_5\cdot OH,$$

that whilst the amount of water produced was theoretically capable of decomposing all the diazomethane formed, its effect was greatly suppressed by the presence of a relatively large volume of alcohol. It may be mentioned that results very similar to those recorded in Expt. 7 were obtained when diazomethane was generated in the presence of pure methyl, propyl, *n*-butyl, and *iso*amyl alcohol respectively. Moreover, since there was no evidence of the formation of an ether ($R\cdot O\cdot CH_3$), it must be concluded that diazomethane does not attack the hydroxyl group of an alcohol.

The chief point of practical interest arising out of these observations lies in the simple application of the reaction as a method for studying the properties of diazomethane under more favourable conditions. In the case of a neutral substance, for example, it may be dissolved in alcohol,* together with a small excess of nitrosomethylurea; on addition of the requisite amount of sodium ethoxide, diazomethane is instantly generated in situ with the substance to be attacked.

Decomposition of Nitrosomethylurea by Ammonia.

When an alcoholic solution of ammonia was added to a similar solution of nitrosomethylurea cooled to 0°, there was vigorous evolution of nitrogen, and a colourless solution was obtained. After a few minutes, a certain quantity of acicular prisms separated, which were identified as ammonium cyanate. As the

* Pure alcohol which has been finally dried by adding to it a small quantity of an ethereal solution of diazomethane may be used with advantage.

temperature was allowed to rise, the crystals redissolved. The primary reaction was as follows:

$$OH\cdot C(:NH)\cdot N(NO)\cdot CH_3 + NH_3 = NH_4OCN \rightleftharpoons CON_2H_4 + N_2 + CH_3\cdot OH.$$

Three experiments gave yields of urea which varied from 42 to 53 per cent. of the theoretical. Methylurea and a small quantity of *as*-dimethylurea (which melted at 181°) were separated from the mother liquors; these were the result of (1) the methylation of ammonia, $CH_2N_2 + NH_3 = CH_3\cdot NH_2 + N_2$, and (2) the further methylation of methylamine to dimethylamine. As the reaction progressed, each amine decomposed a portion of nitrosomethylurea according to the above equation. The further study of these reactions will form the subject of a future communication.

The Spontaneous Decomposition of Nitrosomethylurea.

It may be worth while to point out that no specimen of nitrosomethylurea could be kept unchanged for more than about five months. One preparation (about 30 grams), stocked in a dark brown, glass-stoppered bottle, decomposed spontaneously after 162 days, although only three days previously several grams removed for the preparation of diazomethane behaved in a normal manner. The decomposition was on the lines of the change produced by heat (equation *d*), and whilst much trimethyl *iso*cyanurate was formed, a viscous product freely soluble in water was generated, the nature of which has not yet been elucidated.

The behaviour of a number of other substituted ureas towards nitrous acid is shown below. The experiments were carried out as described under Expt. 1.

	Vol. of N_2 evolved. C.c.	Decomposition according to equation (*a*). Per cent.	Yield of nitroso-derivative. Per cent.
1. Ethylurea	5·3	23·66	76·34
2. *n*-Butylurea.....	7·99	32·60	67·40
3. *iso*Amylurea	11·5	51·33	48·67
4. Benzylurea	12·97	57·90	42·10
5. Phenylurea	14·96	66·78	33·22

Nitrosoethylurea, prepared in a manner similar to the methyl derivative, was obtained in pale buff-yellow, hexagonal plates which melted at 103—104°. Diazoethane was obtained on decomposition with potassium hydroxide according to equation (*e*); ethylene to the extent of 14·77 per cent. of the theoretical was simultaneously formed, thus:

$$(e)\quad OH\cdot C(:NH)\cdot N(NO)\cdot C_2H_5 + KOH = KOCN + C_2H_4 + N_2 + 2H_2O.$$

A very good yield of diazoethane in ethereal solution was readily prepared by the method described under Expt. 5.

Nitroso-n-*butylurea*,* $C_5H_{11}O_2N_3$, formed almost colourless, hexagonal plates which melted at 85°. Diazo-*n*-butane was obtained as an amber-coloured, mobile liquid with a stupefying odour by the direct addition of nitrosobutylurea to 70 per cent. potassium hydroxide solution cooled to 0°; butylene and nitrogen were simultaneously formed to the extent of about 30 per cent. of the theoretical on the lines of equation (*e*).

Nitrosoisoamylurea, $C_6H_{13}O_2N_3$, was obtained in minute, pale buff, unctuous, platy crystals which melted at 74°; since *iso*amylurea is sparingly soluble in water, it was necessary to use 30 per cent. acetic acid as solvent in the preparation of the nitroso-derivative.

Diazoisopentane, $C_5H_{10}N_2$, was obtained as a dark brown oil of unpleasant odour by the addition of potassium hydroxide solution to the nitrosourea.

Nitrosobenzylurea, $C_8H_9O_2N_3$, which was prepared by the action of nitrous acid on benzylurea dissolved in 50 per cent. acetic acid, formed many-sided prisms which melted at 101°; these were insoluble in water, but readily soluble in alcohol or ether.

Phenyldiazomethane, $C_6H_5{\cdot}CH{:}N_2$, separated as a deep reddish-brown oil on the addition of the nitroso-compound to a 70 per cent. solution of potassium hydroxide.

Summary.

(1) The interaction of mono-substituted ureas and nitrous acid in two directions, with (*a*) production of nitroso-derivatives, and (*b*) the complete disruption of the molecule, is explained by the presence in solution of two structural forms of the urea in equilibrium.

(2) The nitroso-derivatives are shown to have the constitution $OH{\cdot}C(:NH){\cdot}N(NO)R$, and their formation is promoted in proportion to the electropositive character of the radicle (R) in the original urea.

(3) The aliphatic nitroso-derivatives are decomposed by alkalis with the production of diazo-derivatives of the paraffins in very good yields.

* n-*Butylurea*, $C_5H_{12}ON_2$, from which the nitroso-derivative was obtained has not been hitherto described. It was readily obtained by evaporating at 100° an aqueous solution of *n*-butylamine hydrochloride and potassium cyanate. It formed crystals which melted at 86° and were readily soluble in water or alcohol.

(4) It is shown that diazomethane and its homologues may be conveniently prepared in alcoholic solution for the study of their reactions.

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[*Received, July 11th*, 1919.]

XCV.—*Dyes Derived from Quinolinic Acid.*

By PRAPHULLA CHANDRA GHOSH.

THE object of the present investigation was to prepare dyes from quinolinic acid analogous to the phthaleins, and to compare their colour and fluorescence. That quinolinic acid condenses with phenol and resorcinol has, indeed, been mentioned by Noelting and Collin (*Ber.*, 1884, **17**, 258), but few details were given, and the products were not analysed. A compound from quinolinic acid and hydroxyquinol has been described by Liebermann and Wölbling (*Ber.*, 1902, **35**, 1786). In the present work, the condensation of quinolinic acid with resorcinol, catechol, phloroglucinol, *m*-phenylenediamine, *m*-dimethylaminophenol, and 2:4-diaminophenol has been effected. These condensations take place without the use of any condensing agent by simply heating the two constituents together.

In comparison with the corresponding phthaleins, the effect of the presence of the nitrogen atom in the ring is to lighten the colour and to diminish the fluorescence. In this series of compounds, the greater the power of an auxochromic group to deepen the colour, the greater is its effect on fluorescence. The compound obtained from quinolinic acid and *m*-dimethylaminophenol has the deepest colour and is the most strongly fluorescent.

Dyes analogous to hydroxyanthraquinones have not yet been prepared, but work in this direction is being continued.

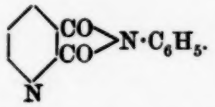
EXPERIMENTAL.

Quinolinic acid was prepared by oxidising a solution of quinoline (10 grams) in acetone (150 c.c.) with a 5 per cent. aqueous solution of the theoretical quantity of potassium permanganate at about 10°.

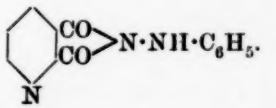
If the manganese dioxide is dried in the air, powdered, and then extracted with alcohol, the solution, on concentration, deposits pale yellow needles melting at 71—72° This substance is insoluble in

alkali hydroxides and volatile with steam. The amount obtained was sufficient only for an estimation of nitrogen:

0·1145 gave 17·6 c.c. N_2 at 31° and 756 mm. N = 17·16 per cent.

Quinolinanil, 

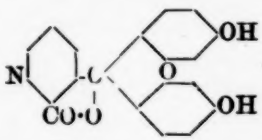
Half a gram of quinolinic acid and 2 c.c. of aniline were heated on the sand-bath for ten to fifteen minutes, when the whole of the acid dissolved. On cooling, crystals separated, which were collected and washed with alcohol. They formed colourless, prismatic needles melting at 248—251° (Engler, *Ber.*, 1894, **27**, 1789, gives 228°) (Found: N = 13·4. $C_{13}H_8O_2N_2$ requires N = 12·50 per cent.).

Quinolinylphenylhydrazine, 

Half a gram of the acid was heated with 2 c.c. of phenylhydrazine for about ten minutes. The clear solution, on cooling, became syrupy, and on adding alcohol, crystals were obtained which, when collected and washed free from phenylhydrazine, melted and decomposed at 237—238°:

0·099 gave 15·9 c.c. N_2 at 31° and 755 mm. N = 17·68.

$C_{13}H_9O_2N_3$ requires N = 17·55 per cent.

Resorcinolquinolinein, 

Two grams of quinolinic acid and 4 grams of resorcinol were heated at 180—200° for two hours. Some violet colouring matter sublimed, which might have been due to the formation of a substance resembling 1:3-dihydroxyanthraquinone. On cooling, the fusion was extracted with alcohol, and the dye was precipitated from the alcoholic extract with water. It could not be crystallised. It melts and decomposes at 266—267°. It is fluorescent in alcohol, acetone, or toluene, and aqueous potassium hydroxide gives an orange-green fluorescence:

0·1020 gave 0·2550 CO_2 and 0·032 H_2O. C = 68·1; H = 3·48.

$C_{19}H_{11}O_5N$ requires C = 68·46; H = 3·33 per cent.

The *silver* salt was prepared in the ordinary way:

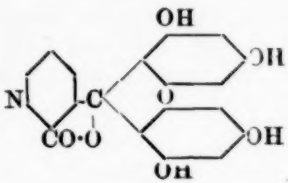
0·2132 gave 0·1092 AgCl. Ag = 38·6.

$C_{19}H_9O_5NAg_2$ requires Ag = 39·5 per cent.

Catecholquinolinein.

This compound has not yet been obtained in sufficient quantity for analysis. It is prepared and purified in the same way as the above compound. It dissolves in aqueous potassium hydroxide with a greenish-blue colour.

Phloroglucinolquinolinein,



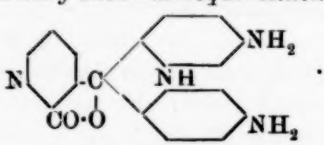
Two grams of quinolinic acid and 4 grams of phloroglucinol were heated at 130—150° for about ten minutes. At first the mixture melted, the colour changing to red, and then the whole solidified. On crystallisation from water, a red compound melting and decomposing at 275—277° was obtained, which was very readily soluble in alcohol:

0·100 gave 0·2277 CO_2 and 0·0289 H_2O. C = 62·1; H = 3·21.

$C_{19}H_{11}O_7N$ requires C = 62·46; H = 3·01 per cent.

If the solid mass is dissolved in alcohol and the solution concentrated, a pale yellow, crystalline compound is obtained which does not melt at 295°. It dissolves in aqueous potassium hydroxide with a yellow colour like the hydroxybenzophenones, and is more readily soluble in water than the compound just described. It has not been obtained in sufficient quantity for analysis.

m-*Phenylenediaminequinolinein,*



One gram of quinolinic acid and 3 grams of *m*-phenylenediamine hydrochloride were heated slowly to 210° and kept at 210—220° for twenty to twenty-five minutes. After cooling, the mass was extracted with alcohol and filtered; the solution was fluorescent.

The dye was obtained in a pure state by adding ether to the alcoholic solution. It melts and decomposes at 232—235°:

0·103 gave 15·4 c.c. N_2 at 30° and 758 mm. N = 16·73.

$C_{19}H_{14}O_2N_4$ requires N = 16·97 per cent.

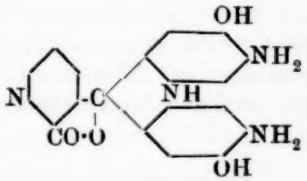
m-*Dimethylaminophenolquinolinein*,

Quinolinic acid (0·75 gram) and *m*-dimethylaminophenol (1·5 grams) were heated at 120—130° for fifteen to twenty minutes, and then the temperature was slowly raised to 150°, when heating was stopped. The mass was extracted with alcohol, and the dye precipitated from the solution with water. When crystallised from dilute alcohol, it melted and decomposed at 148—151°. The alcoholic solution shows a reddish-violet fluorescence, which is deeper in acetic acid or alcoholic hydrochloric acid:

0·1062 gave 10·8 c.c. N_2 at 32° and 751·4 mm. N = 11·1.

$C_{21}H_{21}O_3N_3$ requires N = 11·5 per cent.

2:4-*Diaminophenolquinolinein*,



One gram of quinolinic acid and 3 grams of 2:4-diaminophenol hydrochloride were slowly heated to 180° and kept at this point for a few minutes. The dye was extracted by boiling with alcohol and filtering from the unchanged diaminophenol hydrochloride. It was purified by dissolving in alcohol and precipitating with water, but could not be crystallised. It does not melt at 290°. The compound is reddish-brown, and its solution in alcohol is fluorescent:

0·101 gave 13·8 c.c. N_2 at 30° and 756 mm. N = 15·37.

$C_{19}H_{14}O_4N_4$ requires N = 15·47 per cent.

In conclusion, I beg to express my great indebtedness to Sir P. C. Rây for the loan of 200 grams of quinoline.

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[*Received, July* 31*st*, 1919.]

XCVI.—*Sodium Hypochlorite.*

By Malcolm Percival Applebey.

Sodium hypochlorite in a solid form was first obtained by Muspratt and Shrapnell Smith, of the United Alkali Co., Ltd., in the course of investigations directed towards the preparation of very concentrated solutions (*J. Soc. Chem. Ind.*, 1898, **17**, 1096; 1899, **18**, 210; 1903, **22**, 591). Their preparations were obtained by cooling concentrated solutions, and had a composition corresponding approximately with a hexahydrate. The product melted in its water of crystallisation at 20°, and the fusion was unstable. It could be dehydrated slowly by means of a current of dry air under diminished pressure, and had then a melting point of 45°, but the results were deemed to be of no commercial value, and the investigations were accordingly discontinued.

It was suggested by Mr. Muspratt that a complete investigation of the hydration and solubility relationships might furnish information of both scientific and industrial value, and a preliminary survey of the field has accordingly been made. This has already yielded results of some importance, which are the subject of this communication. They are to be regarded as provisional, and will be followed at a later date by a systematic phase-rule treatment.

Preparation and Properties of Muspratt's Hydrate.

The hypochlorite solutions were prepared by treating 35 per cent. sodium hydroxide solution cooled in ice-water with chlorine, removing the precipitated sodium chloride, adding sodium hydroxide equivalent to the sodium chloride separated, and repeating the treatment with chlorine until the solution was about 5*N* when tested with neutral sodium arsenite solution. On a few occasions, preparations were lost owing to spontaneous transformation to chlorate and chloride. Such transformation, when it sets in, takes place with extreme rapidity in concentrated solutions, and is accompanied by the evolution of considerable quantities of gas consisting of both chlorine and oxygen. The transformation to chlorate can, however, be prevented by observing the three conditions laid down by Muspratt and Shrapnell Smith, namely, (1) low temperature; (2) absence of iron or other heavy metals which act as catalysts; (3) presence of excess of free alkali. The solution, which has been freed from precipitated sodium chloride, is

now cooled to about $-10°$ in a freezing mixture and induced to crystallise, either by shaking or by impregnating with a crystal from a previous preparation. The hypochlorite then separates as a mass of very fine, hair-like crystals filling the whole liquid, whilst the temperature rises considerably. When the whole has again reached the temperature of the freezing mixture, the crystals are separated from the mother liquor by suction through a Büchner funnel without filter paper or asbestos, the form of the crystals being such as to make their retention easy. The crystals are pressed down to remove adhering mother liquor, and then appear to be colourless at the top, although the mass in the lower part of the funnel is green, owing to the presence of mother liquor, which cannot be entirely removed, being formed anew by deliquescence during filtration. The crystals liquefy at temperatures varying between 18° and 19°, according to their purity. The fusion is not quite transparent, but becomes so at a somewhat higher temperature. This behaviour, in conjunction with the subsequent separation of a lower hydrate on cooling, appears to show that the hydrate does not melt completely, but undergoes a transformation at about 19° to a lower hydrate, formed in very small quantity, and its saturated solution, which has almost the same composition as the original crystals.

Analysis of the crystals gave somewhat unsatisfactory results, since, owing to the low melting point and rapid deliquescence, it was difficult to secure a sample in a sufficiently dry state. After several trials, it was found best to filter off a small quantity in a Gooch crucible without asbestos, and to break up the crystals in the crucible with a spatula while the suction continued. All attempts to dry the crystals with filter paper failed, owing to the rapid oxidising action on the paper, which resulted in the development of heat, and after a time led actually to charring of the paper. For analysis, the substance was weighed out and dissolved in water, and aliquot parts of the solution were titrated against arsenite for active chlorine and against silver nitrate and thiocyanate for total chlorine after reduction of the hypochlorite with the correct amount of arsenite solution. The following analytical data refer to two specimens which gave for total chlorine quantities not greater than would be formed from the hypochlorite present, and were therefore free from chloride:

Sample I, prepared by twice recrystallising after fusion:

1·1147 gave active chlorine 0·4065 = 36·47.

H_2O (by difference) 0·6899 = 62·07.

Sample II, prepared by synthesis from the pentahydrate:

0·5020 gave active chlorine 0·1807 = 35·99.

H_2O (by difference) 0·3123 = 62·21.

$NaOCl,7H_2O$ requires active chlorine = 35·36. H_2O = 62·88 per cent.

$NaOCl,6H_2O$ requires active chlorine = 38·85. H_2O = 59·21 per cent.

From these data, it would appear that Muspratt's hydrate is nearer in composition to a heptahydrate than to a hexahydrate. At the same time, the agreement with the heptahydrate formula is by no means good, and it may be found on further investigation that more than one hydrate is present in the crystals prepared by Muspratt's method.

Sodium Hypochlorite Pentahydrate.

When the cloudy liquid obtained by heating the heptahydrate to 20° is allowed to cool slowly to the ordinary temperature, large and well-formed crystals of a new hydrate are obtained. The crystals are greenish-yellow, and contain a considerable amount of mother liquor; when they are broken up in an agate mortar, a separation of liquid takes place, and the powdered substance must be freed from this liquid by filtration through a Gooch crucible.

When prepared in this way, the substance gave the following analytical results:

	I.	II.	Calculated for $NaOCl,5H_2O$.
Weight of substance	0·3482 gram	0·3786 gram	—
Active chlorine	0·1473 „	0·1615 „	—
„ „ per cent. ...	42·32	42·66	43·10
Cl as chloride	0·0006	nil	—
Water (by difference)	0·1929 gram	0·2090 gram	—
„ per cent.	55·40	55·20	54·75
Loss on heating	63·51	—	64·47

The pentahydrate melts at 27°, and is thus a much more practicable substance than the heptahydrate. The fusion is in this case also somewhat cloudy, but the nature of the suspension cannot yet be definitely stated. Up to the present, a small amount of decomposition has always taken place during melting. The pentahydrate is very deliquescent, but the crystals are not unstable at the ordinary temperature if kept in a well-stoppered bottle; a specimen kept for more than a week in a corked test-tube in a well-lighted laboratory showed no measurable increase in chloride content, although some deliquescence had taken place.

The mother liquor from which the pentahydrate has separated

may be made to give a further yield of pentahydrate by freezing out heptahydrate, heating the latter to 20°, and allowing to crystallise as before. By this procedure, there is no difficulty in converting at least 50 per cent. of the heptahydrate into the corresponding amount of pentahydrate.

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[*Received, August 6th*, 1919.]

XCVII.—*Capsaicin. Part I.*

By ARTHUR LAPWORTH and FRANK ALBERT ROYLE.

CAPSAICIN, the pungent principle of the fruit of various species of the genus *Capsicum*, was first isolated in crystalline form by Thresh (*Pharm. J.*, 1876, [iii], **7**, 21, 259, 473; 1877, **8**, 187) and assigned by him the formula $C_9H_{14}O_2$. Micko (*Zeitsch. Nahr. Genussm.*, 1898, 818) showed that the substance contained nitrogen, and as a result of analyses and molecular-weight determinations deduced the formula $C_{18}H_{28}O_3N$.

Thresh showed that capsaicin is a phenol, but did not discover any other very marked chemical characters; Micko, whose contributions are probably of most importance amongst those of subsequent investigators, established the fact that the molecule of capsaicin contains one phenolic hydroxyl group and one methoxyl group, and this, on the basis of his empirical formula, leads to the expression $C_{17}H_{24}ON(OH)(O{\cdot}CH_3)$ for the substance. Micko prepared the indifferent benzoyl derivative and observed that under certain conditions capsaicin undergoes slight decomposition, emitting a faint odour reminiscent of vanillin.

A comprehensive bibliography of the subject is given in Thorpe's "Dictionary of Applied Chemistry" (1913, **4**, 559).

The present authors began the investigation of the subject in 1914, at which time the only significant data bearing on the chemical nature and structure of capsaicin were the facts above cited. Their study was greatly retarded by other work arising out of the war, and in view of this fact, and especially as the active interest in compounds with pungent characters has been manifested in countries where scientific research has had no such serious setback as here, it is thought desirable to place on record the progress which has now been made.

The authors have examined various methods previously used for isolating pure capsaicin from the crude extract made from the seeds

and have worked out a process which combines a number of devices some of which are based on details of the processes suggested by previous workers, but as a whole appears especially simple in practice.

The properties of capsaicin which have been described by Thresh, Micko, and by Nelson (*Chem. News*, 1911, **103**, 111) have been confirmed in all essential details, but the analyses made have consistently pointed to the formula $C_{18}H_{27}O_3N$ or

$$C_{17}H_{23}ON(OH)(O\cdot CH_3),$$

and not that proposed by Micko, which contains one more atom of hydrogen and is inconsistent with the normal valencies of these four elements in carbon compounds.

The methyl derivative, $C_{17}H_{23}ON(O\cdot CH_3)_2$, hereafter termed methylcapsaicin, has been prepared and characterised; it is non-phenolic and is much less pungent than the parent substance.

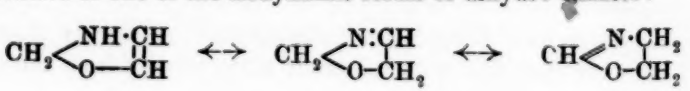
Both capsaicin and methylcapsaicin are feebly basic. They are extremely stable towards hot concentrated alkali hydroxides, but are very slowly attacked by hot acids; the products of hydrolysis have not been determined, but ammonia is always one of them, methylamine being entirely absent. The action of phosphorus pentachloride on methylcapsaicin yields a small quantity of a volatile, nitrogenous oil; this the authors suspect to be the nitrile of a fatty acid, but have not yet had the opportunity of examining it closely.

Most attention has been paid, in the first instance, to the action of reducing agents, many of which evidently attacked capsaicin to a certain extent (as was evidenced by the ready formation of ammonia or ammonium salts), without any obvious general destruction or charring.

From the more highly purified capsaicin, reduced by means of sodium and ethyl alcohol, ammonia was obtained and also, among other products, a small quantity of a compound, the bulk of which boiled at about 216—217° and had the odour and general properties of a fatty alcohol.

Oxidation of methylcapsaicin takes place readily, and among other products veratric acid, $C_6H_3(OMe)_2\cdot CO_2H$, was the most readily recognised. There was also formed a fatty acid, of which scarcely sufficient was obtained to identify with complete certainty.

Even disregarding such of the above considerations as are yet not fully substantiated, it is probable that capsaicin is a *C*-disubstituted derivative of one of the isodynamic forms of dihydro-oxazole:



Experimental.

Isolation of Capsaicin.

The ordinary alcoholic extract of capsicums consists mainly of gum or dextrin-like compounds, soluble in water, together with substances which have the characters of saturated and unsaturated carboxylic acids, and relatively small amounts of fats.

In order to isolate capsaicin from this mixture advantage is taken of the fact that capsaicin does not form a stable barium salt when it is brought into contact with aqueous barium chloride which has been rendered ammoniacal. In the same circumstances, however, the free carboxylic acids present in the extract are mainly precipitated as barium salts which are for the most part insoluble in water, alcohol, or ether, or, more especially, in acetone. The gum-like substance present remains dissolved in the water, which retains only traces of capsaicin easily recovered by extraction with ether, and the bulk of the active principle, together with the fats, is found in the precipitate. On extraction of the precipitate with alcohol or ether the capsaicin and fats dissolve, whilst the bulk of the barium salts are insoluble. These operations, by eliminating the dextrin and fatty acids, effect a great reduction in the bulk of material to be handled.

The following are the details of this part of the isolation process which the authors have applied to numerous samples of extract of West African capsicums kindly prepared for them by Messrs. James Woolley, Sons and Co., of Manchester.

The extract (450 grams) is mixed with hot water (900 c.c.) and ammonia (25 c.c.; D 0·880) previously diluted with several times its bulk of cold water. On stirring, the whole forms an apparently homogeneous solution; it is heated on the water-bath and 90 grams of finely powdered hydrated barium chloride are sifted in very slowly with constant stirring. At this stage the liquid, which contains much brown, semi-fluid deposit, and should have a strong odour of ammonia, is allowed to cool and is separated mechanically from the bulk of the insoluble deposit, filtered, and extracted with ether. The ether is further utilised to extract the deposit, although the latter is subsequently washed several times with fresh ether in order to secure the whole of the contained capsaicin. The united ethereal extracts are evaporated and provide usually about 50—80 grams of "concentrated extract" of capsaicin.

The most satisfactory method of proceeding to the isolation of capsaicin from this "concentrated extract" is to subject it at once to treatment with methyl-alcoholic barium hydroxide in order to

destroy impurities of fatty nature. For this purpose the extract is dissolved in several times its weight of methyl alcohol, the solution heated to boiling, and finely powdered barium hydroxide sifted in at intervals until the solution remains alkaline without further addition after several hours' boiling. Glacial acetic acid is now added cautiously until the solution has permanently lost all alkalinity (towards phenolphthalein), when the methyl alcohol is removed by distillation. The residue is now extracted repeatedly with dry acetone, and the latter recovered by evaporation, when the residue contains practically the whole of the capsaicin which was present in the original extract. A repetition of the last process of extraction with dry acetone is perhaps as a rule desirable, as the whole success of the application of this solvent for the removal of barium salts depends on the exclusion of moisture, which is not easy to secure in the first operation.

The residue still contains traces of impurities of both neutral and acid character. It is subjected to treatment similar to that applied by Thresh to a much more impure material (*Pharm. J.*, 1876, [iii], **7**, 260), that is to say, it is dissolved in aqueous sodium hydroxide (5 per cent.), the solution extracted with ether to remove traces of neutral material and then saturated with carbon dioxide, when the precipitate is isolated by extraction with ether. The precipitate yields capsaicin in crystalline form most readily by a device also employed by Thresh and applied by the present authors as follows:

Crude capsaicin (10 grams) is dissolved in aqueous sodium hydroxide (100 c.c. of 2 per cent.) and warmed on the water-bath until the temperature is about 60°. A warm saturated solution of ammonium chloride is then gradually added until a permanent turbidity is produced. On cooling, crystalline capsaicin is deposited, and may be collected. The mother liquor is again treated with ammonium chloride solution until the deposition of capsaicin ceases.

Properties of Capsaicin.

Many of the more evident properties of capsaicin have already been described by previous workers, and in view especially of the accurate descriptions given by Micko (*loc. cit.*) and Nelson (*loc. cit.*) only a few additional notes are necessary here.

The most highly purified specimens of capsaicin melted at 64—65°. The substance appears to be optically inactive; a solution containing 1·2146 grams dissolved in benzene and made up to 20 c.c. showed no appreciable rotatory power in a 2-dcm. tube at 15°.

Analyses of several pure samples were carried out: Found: C=71·02, 70·97, and 70·88; H=8·90, 8·85, and 9·01; N=4·7.

$C_{18}H_{27}O_3N$ requires C=70·82; H=8·85; N=4·6.

$C_{18}H_{28}O_3N$,, C=70·59; H=9·15; N=4·6.

$C_{18}H_{29}O_3N$ requires C=70·35; H=9·44; N=4·6 per cent.

For the determination of hydroxyl, 0·2437 gram was treated with magnesium methyl iodide in amyl ether, 23·2 c.c. of methane were evolved at 70° and 770 mm.; whence OH=5·3, the theoretical percentage being 5·6.

Capsaicin is sparingly soluble in concentrated hydrochloric acid, and the saturated solution deposits it in crystals on the addition of water. It is scarcely affected when boiled for several hours with 50 per cent. aqueous sodium hydroxide, but is appreciably decomposed after several hours' heating with concentrated hydrochloric acid.

Methylcapsaicin, $C_{17}H_{23}ON(O{\cdot}CH_3)_2$.

This compound is prepared by dissolving capsaicin and methyl sulphate in methyl alcohol and then slowly adding excess of a solution of sodium hydroxide while the whole is kept cool. After half an hour or more the bulk of the solvent is removed, the neutral methylcapsaicin separated from the residual aqueous solution by filtration or by extraction with ether, washed, and crystallised from dilute alcohol.

Found: C=71·39; H=9·16.

$C_{19}H_{29}O_3N$ requires C=71·47; H=9·09 per cent.

Methylcapsaicin dissolved readily in most of the ordinary organic media with the exception of cold light petroleum; it is insoluble in water or alkali hydroxides. It crystallises from dilute alcohol in slender, silky needles melting at 74°, and is much less pungent than capsaicin.

This derivative appears to be slowly altered by boiling with acetyl chloride and it reacts with phosphorus pentachloride below 100°, yielding an oil containing nitrogen, which is volatile in steam and has an odour suggesting that of many nitriles. The authors propose to study the products of this reaction in greater detail in the near future. Methylcapsaicin does not appear to react with phenylhydrazine, and it is recovered unaltered after prolonged boiling with alcoholic hydroxylamine acetate.

Reduction of Capsaicin.

Both capsaicin and its methyl ether are attacked by many comparatively mild reducing agents, but, as a rule, imperfectly. Am-

monia is always one of the products of change, but methylamine has never been detected even in traces. Numerous experiments have been made with the object of identifying the main products, but owing to the small quantities of capsaicin attacked the results were not very decisive. In one experiment, however, 10 grams of capsaicin were treated with a very large excess of metallic sodium in boiling alcohol; the dissolved sodium was precipitated from the resulting solution as carbonate with the aid of a stream of carbon dioxide and the bulk of the solvent removed by distillation through an efficient still-head. Ammonia, free from all traces of methylamine, passed over with the alcohol. From the residue in the still there was isolated without great difficulty nearly half of the capsaicin originally taken and also a small quantity of a liquid, volatile in steam, having a somewhat fragrant odour of higher fatty alcohols. The bulk of this liquid boiled at about 216—217°. As the quantity obtained did not admit of purification for analysis the fraction 216—217° was oxidised by means of dichromate and sulphuric acid mixture; the resulting fatty acid was extracted with ether, boiled with thionyl chloride, and the product shaken with concentrated aqueous ammonia. The amide of the acid was obtained in this way, and after recrystallisation from water appeared as silvery leaflets melting at 98—100°.

Oxidation of Methylcapsaicin with Potassium Permanganate.

Pure methylcapsaicin (10 grams) was dissolved in 3 litres of acetone and finely powdered potassium permanganate was very gradually added until a permanent pink tinge persisted in the solution—this operation occupied about two days—the temperature of the solution never being allowed to exceed 25°. The manganese dioxide was filtered off and washed repeatedly with acetone, the washings being added to the main filtrate and then evaporated.

The residue so obtained, which consisted of a viscid, reddish-brown, semi-solid oil, was subjected to steam distillation from acid solution. The distillate contained a very small quantity of a fatty acid, which was isolated in the usual manner; it was converted into its amide and gave a crystalline product, which melted at 98—99° and was apparently identical with that obtained from the oxidation of the alcohol referred to in the previous experiment, but the yield was extremely small and did not amount to more than 0·05 gram.

The residue, non-volatile in steam, was rendered alkaline with sodium carbonate and then extracted with ether. The ethereal solution yielded slightly more than 5 grams of unchanged methylcapsaicin. The sodium carbonate solution after removal of the methyl-

capsaicin gave nearly 2 grams of an acid, which readily crystallised from hot water in hard, flat needles melting at 179—180°. This acid yielded a chloride melting at 69° and an amide melting at 163°. Veratric acid, chloride, and amide melt at 70° and 164° respectively, and when mixed with the above products from methylcapsaicin were unchanged in melting point. The acid was dried in the steam-oven and analysed. (Found, C=59·4; H=5·4. $C_9H_{10}O_4$ requires C=59·3; H=5·5 per cent.)

There is therefore no doubt that the acid was veratric acid.

Oxidation of Methylcapsaicin with Chromic Acid.

Methylcapsaicin was oxidised by a boiling solution of chromic acid in dilute sulphuric acid. The liquid was then subjected to a current of steam and oily drops passed over. The whole of the distillate was rendered alkaline with sodium carbonate and evaporated almost to dryness; it was then carefully acidified and an oily acid was liberated which was extracted with ether. The product had a strong odour of acetic acid and was therefore exposed over solid potassium hydroxide in a desiccator for several days. The odour of the acetic acid disappeared and gave place to a rather pleasant one recalling that of *n*-nonoic acid. The colourless oil ultimately obtained was cooled in ice-water, when it readily solidified to a crystalline mass which melted sharply at 12° (nonoic acid melts at 12·5°). It also yielded an amide melting at 98—99°, which was in no respect distinguishable from the amide of *n*-nonoic acid prepared from the pelargonic acid of commerce.

The investigation is being continued.

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NOTE.—Since the work recorded in the foregoing pages was completed, the authors' attention was called to the paper by Nelson (*J. Amer. Chem. Soc.*, 1919, **61**, 1115), which renders certain of their previous views obsolete.

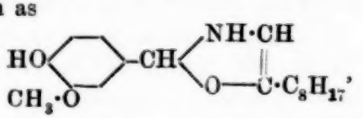
Inter alia, Nelson has obtained from capsaicin by the action of acids and alkalis under pressure vanillylamine and a decylenic acid, the latter having a branched chain. He concludes that capsaicin is a condensation product of vanillylamine and a decylenic acid.

The present authors at first suspected that the fatty acid repeatedly referred to in their own communication was identical with this decylenic acid. They obtained their acid in very small

quantities, and the quantity of amide available for a combustion was only 0·0921 gram (Found, C = 68·7; H = 12·3. $C_9H_{19}ON$ requires C = 68·8; H = 12·1 per cent.), whilst its properties as well as those of its amide closely resembled those of *n*-nonoic acid; thus when super-cooled the acid at once solidified when seeded with *n*-nonoic acid, and the amide, as already mentioned, could not be distinguished by appearance or by a mixed melting-point determination from the amide of *n*-nonoic acid.

Since the authors' attention was called to Nelson's work, the supposed nitrile obtained directly from methylcapsaicin by the action of inorganic acid chlorides has successfully been converted by means of hydrogen peroxide and dilute sodium hydroxide at 40° into an acid amide melting at 98—100°.

The present authors are not fully disposed to accept Nelson's view of the constitution of capsaicin as final. His conception of capsaicin as an acid amide is not easily reconciled with the somewhat ready reduction of a part of capsaicin to ammonia and an aliphatic alcohol boiling at about 216—217°; its distinctly basic character and the great stability of the substance towards alkalis are also somewhat difficult to understand. They originally hazarded the view that capsaicin was probably a derivative of dihydro-oxazole, and the possibility is not wholly excluded that capsaicin is built with a ring structure such as



for under the energetic conditions used by Nelson internal oxidation or molecular rearrangement would not be surprising.

XCVIII.—*The Vapour Pressures and Densities of Mixtures of Acetone and Methyl Ethyl Ketone.*

By Tudor Williams Price.

Much work, both theoretical and practical, has been done on the vapour pressures of binary mixtures, notably by Duhem, Lehfeldt, Ostwald, Roozeboom, Zawidski, and Young. It has been shown that for binary mixtures the components of which are miscible in all proportions, the vapour pressure at any one temperature may lie between those of the components; it may be higher or lower than that of either component.

If, however, the two components are closely related, the curvature of the graph, representing the relation between vapour pressure and concentration for any particular temperature, should not be great. According to Guthrie (*Phil. Mag.*, 1884, [v], **18**, 517), if there is no heat or volume change on mixing the two components, the relation between vapour pressure and percentage composition by weight, expressed graphically, should be a straight line, but this does not generally hold.

Van der Waals (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 170) considers that, if the critical pressures of the two substances are equal or nearly so, and if the molecular weight of each is normal in both the liquid and gaseous states, and if the relation suggested by Galitzine and by Berthelot holds good, that is, if $a_{1\cdot 2}=\sqrt{a_1 \cdot a_2}$, where $a_{1\cdot 2}$ represents the attraction of the unlike molecules, and a_1 and a_2 the attraction of the like molecules, then the relation between the vapour pressure and molecular composition should be represented by a straight line, that is,

$$P=\frac{p \cdot P_A+(100-p)P_B}{100},$$

where P, P_A, and P_B are the vapour pressures of the mixture and the two components A and B at the same temperature, and p is the molecular percentage of liquid A in the mixture.

This relation has been verified many times, notably by Young, for mixtures such as chlorobenzene and bromobenzene, which are closely related. When the components are very closely related, but have different critical pressures, the percentage difference between the observed and calculated pressures $\frac{100\,P'-P}{P}$ for the mixtures at any temperatures is very small, even when there is molecular association in the liquid state, as with methyl and ethyl alcohol.

During the course of experiments on the production of cordite, using methyl ethyl ketone as substitute in whole or in part for acetone as the gelatinising agent, it was found that some abnormalities were obtained in the volatility of the samples. For example, a cordite gelatinised by a mixture of equal proportions by weight of acetone and methyl ethyl ketone had a lower volatility than cordite made with acetone or with methyl ethyl ketone. This showed that the cordite gelatinised with the mixed solvent dried quicker than the others, presumably owing to the fact that the 50 per cent. mixture of acetone and methyl ethyl ketone has a greater vapour pressure than either of its two components.

This supposition, although unlikely because of the close relation-

ship between acetone and methyl ethyl ketone, is not outside the bounds of possibility, owing to the great difference between their critical pressures, which are given as 52·2 and 60·0 atmospheres for acetone (Sazotschewsky, in Landolt and Bornstein's "Tabellen") and 47·5 atmospheres for methyl ethyl ketone (Grassi, *Nuovo Cim.*, 1914, [vi], **7**, i, 313).

It was recognised that vapour-pressure measurements of the pure solvents and their mixtures would not furnish an absolute guide to the rate of escape of solvent from cordite on drying, because of the colloidal nature of the latter, but it was thought that such measurements would throw some light on the abnormal behaviour of cordite made with mixed solvent when being dried. Accordingly, a series of vapour pressure determinations were carried out, the results of which are given below.

Experimental.

Materials.—The acetone was prepared from commercial acetone as follows. After drying and fractionation, it was treated with sodium iodide according to Shipsey and Werner's method (T., 1913, **103**, 1255). The white, needle-shaped crystals of the additive compound, $NaI,3C_3H_6O$, were quickly collected, pressed between blotting-paper, and transferred to a dry distilling flask. On gently warming, the acetone distilled over. The distillate was dried over fused calcium chloride for twenty-four hours and distilled through a five-bulb column. The fraction 56·15—56·25°/760 mm. was collected separately, dried again over fused calcium chloride for twenty-four hours, and fractionated as before. Practically all distilled constantly at 56·2°/760 mm. (corr.).

A sample gave the following results on analysis:

Acidity as CO_2	= 0·0012 per cent.
,, ,, acetic acid	= Nil.
Alkalinity as $N/10$-H_2SO_4 c.c.	= Nil.
Turbidity with water	= Nil.
Residue on evaporation	= 0·0003 per cent.
Permanganate test	= 50 minutes.

The methyl ethyl ketone was freed from acetone by two washings with saturated brine, in which it is not very readily soluble. The purified ketone was dried over fused calcium chloride and fractionated through a five-bulb column. The fraction distilling at 78—80° was dried and fractionated again. From this second distillation, a fraction boiling at 79—80° was collected separately, dried,

and again fractionated. In this way, a final fraction was obtained boiling at 79·5—79·6°/759 mm. (corr.). The boiling point of methyl ethyl ketone is given as 79·57°/760 mm. (Marshall, T., 1906, **89**, 1375).

A sample gave the following tests on analysis:

Aldehydes	=	Nil.
Acidity as CO_2	=	0·0002 per cent.
Alkalinity as $N/10$-H_2SO_4 c.c.	=	Nil.
Permanganate test	=	20 minutes.

The liquids were kept in tightly stoppered bottles in a dark cupboard.

Apparatus.—The apparatus used was designed by Mr. Allan Morton (*private communication*).

It consisted of two similar barometer tubes connected at the bottom by a T-piece to each other and to a mercury reservoir, which could be raised or lowered at will. The top of each tube was sealed to a piece of capillary tube, longer than the barometer tube, which was bent over parallel to the barometer tube to which it was sealed. The bottom of each capillary tube was bent over again and dipped into small cups of mercury.

The barometer tubes were surrounded by a wide glass tube containing water, which was circulated and stirred by compressed air and kept at a constant temperature.

The method of procedure was as follows. Recently boiled mercury was placed in the reservoir, which was then raised until the mercury filled the barometer tubes and the capillaries and overflowed into the cups. The reservoir was then lowered and the mercury column broke at the junction of the capillaries with the barometer tubes, thus forming a vacuum in the latter. This was repeated until no air was left in the tubes and a perfect vacuum obtained.

The liquid the vapour pressure of which was to be measured was then placed above the mercury in one of the small cups. The mercury reservoir was raised until mercury overflowed into the cups. The cup with the liquid was then moved until the end of the capillary was in the liquid above the mercury. On lowering the reservoir, some of this liquid was drawn into one of the barometer tubes. By this means, the latter contained the necessary liquid and its vapour, whilst the other tube acted as a barometer.

A slight modification was found to be necessary for accurate work. As described by Morton, the capillary tubes are outside the water-jacket, and are consequently at a lower temperature than the observation tube. Liquid from the observation tube therefore

distils over and condenses above the mercury in the capillary tube, thus causing an appreciable alteration of the concentration in the case of a mixture. This difficulty was overcome by making the water-jacket wider, so as to contain the capillary tubes and to keep them at the same temperature as the observation tube.

Two thermometers were used in the work, one reading from 0° to 50° in tenths, and the other from 50° to 100° in tenths. These were carefully standardised by comparison with thermometers which had recently been tested at the National Physical Laboratory, and could easily be read to 0·01°. The temperature of the water surrounding the observation tubes was kept constant to within 0·05°, and all readings of the mercury and solvent levels were taken through a cathetometer.

A quantity of liquid remained in the observation tube above the mercury, and for this a correction had to be applied, obtained from the densities of the mixtures at the required temperature.

The densities were determined in a Regnault specific gravity bottle for liquids, of about 50 c.c. capacity, fitted with a capillary stem widening out into a cup-shaped reservoir fitted with a ground-glass stopper. All weighings were done on a balance sensitive to 0·0001 gram with standardised brass weights, and in the neighbourhood of 760 mm. pressure, and hence no correction was made for changes in atmospheric pressure. The balance case was kept dry by means of dishes containing calcium chloride, so that no correction was made for the relative humidity of the air.

A counterpoise of the same kind of glass and of the same shape as the specific gravity bottle was used in all weighings, and all weights were reduced to a vacuum.

The thermostat was provided with a thermoregulator and mechanical stirrer, and could be kept at the desired temperature within 0·05°.

For the pure liquids, determinations were made in duplicate; these agreed very closely, and the mean is given. For the mixtures, determinations were carried out in duplicate on the same solution, there being not sufficient material to make up two separate solutions of the same concentration.

Results.—The vapour pressures obtained are given in table I. Each figure is the mean of three or four determinations at the same temperature, which agreed very closely.

TABLE I.

Vapour Pressures of Mixtures of Acetone and Methyl Ethyl Ketone at Various Temperatures.

Composition of mixture.		Vapour pressure in mm. at following temperatures.						
Percentage of acetone by weight.	Molecular percentage of acetone.	20°	25°	30°	35°	40°	45°	50°
100	100	186·3	232·0	284·6	348·1	425·3	510·8	620·9
75	78·83	167·8	—	255·5	—	379·1	—	548·2
62·5	67·42	161·8	—	243·3	—	354·0	—	508·4
50	55·38	155·5	—	226·5	—	327·8	—	469·7
37·5	42·69	141·3	—	205·8	—	299·6	—	430·2
25	29·27	125·5	—	183·5	—	267·4	—	388·1
12·5	15·06	109·9	—	160·6	—	234·2	—	341·9
0	0	77·5	98·4	121·4	151·0	188·4	252·9 (at 46·5°)	300·0

These results are shown graphically in Figs. 1 and 2. Fig. 1 shows the relation between vapour pressure and concentration (by weight) over the whole range from pure acetone to pure methyl ethyl ketone at the temperatures indicated, whilst Fig. 2 shows the relation between vapour pressure and temperature for the pure substances and all the mixtures.

The densities are given in table II.

TABLE II.

Densities of Mixtures of Acetone and Methyl Ethyl Ketone at Various Temperatures.

Composition of mixture.		Density at following temperatures.			
Percentage of acetone by weight.	Molecular percentage of acetone.	20°/4.°	30°/4°.	40°/4°.	50°/4°.
100	100	0·79082	0·77931	0·76784	0·75599
75	78·83	0·79428	0·78311	0·77181	0·76020
62·5	67·42	0·79603	0·78495	0·77368	0·76233
50	55·38	0·79782	0·78677	0·77567	0·76439
37·5	42·69	0·79956	0·78869	0·77776	0·76664
25	29·27	0·80135	0·79061	0·77982	0·76877
12·5	15·06	0·80314	0·79249	0·78173	0·77084
0	0	0·80495	0·79442	0·78391	0·77315

Discussion of Results.—The accuracy of the results obtained in the vapour pressure measurements may be gauged by comparing them with results obtained by other workers. Table III affords a comparison of the various results given for acetone.

TABLE III.

Showing Results obtained for the Vapour Pressure of Acetone by Various Workers.

Temperature	Vapour pressure of acetone in mm. of mercury.			
	Author.	Regnault.[1]	Sameshima.[2]	Taylor.[3]
20°	186·3	179·6	184·8	182·5
25	232·0	—	229·2	229·0
30	284·6	281·0	282·7	281·0
35	348·1	—	346·4	343·0
40	425·3	420·2	421·5	416·0
45	510·8	—	510·5	505·0
50	620·9	620·9	612·5	607·0

[1] Obtained from Landolt and Bornstein's "Tabellen."
[2] *J. Amer. Chem. Soc.*, 1918, **40**, 1482.
[3] *J. Physical Chem.*, 1900, **4**, 436.

The agreement between the present results and those of Sameshima is good, except at 50°, at which temperature better agreement is obtained with Regnault.

The results show, however, that the apparatus is capable of giving accurate results, and does away with the necessity of using stopcocks, with their attendant troubles due to leakiness and the presence of grease. The chief source of error is the possibility of the liquid absorbing air before being carried over into the observation tube. With pure liquids, this possibility can be obviated to a large extent by boiling immediately before introduction, but with mixtures this procedure would alter the concentration, and hence the above possibility must not be neglected.

As regards methyl ethyl ketone, no figures have been found in the literature for the vapour pressure at temperatures between 20° and 50°.

An examination of Fig. 1 shows that the vapour pressure–concentration curves lie between the vapour pressures of the two components at all temperatures, thus negativing the suggestion that there might be a mixture of acetone and methyl ethyl ketone having a higher vapour pressure than either component. Hence the explanation of the abnormality of the volatility of cordite gelatinised with a mixture of equal parts of acetone and methyl ethyl ketone, based on the above suggestion, is unfounded.

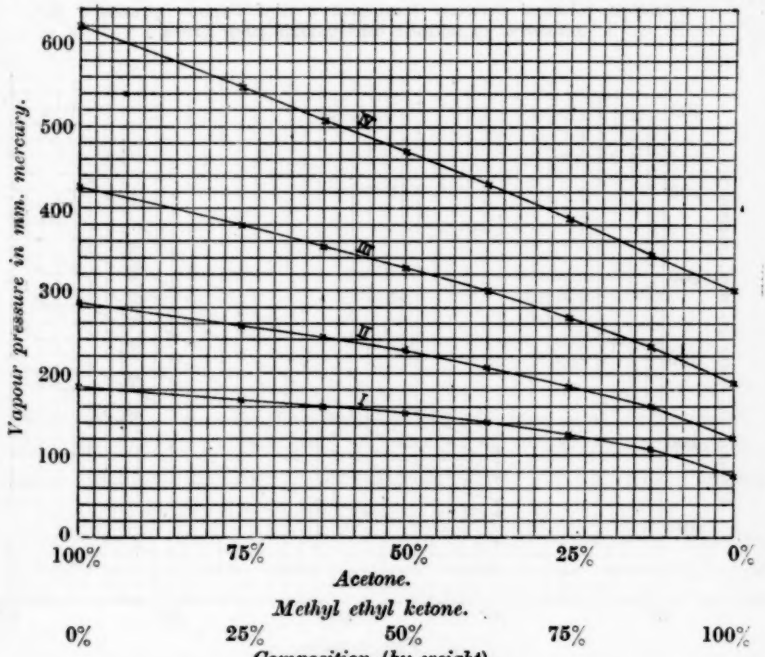
The graphs in Fig. 1 are not straight lines, but they approximate thereto, and this approximation is nearer as the temperature is increased. The deviation from a straight line, for the curve at 50°, is given in table IV by comparing the observed vapour pressures of the mixtures with those calculated according to the expression

$$\frac{P = m.P_A + (100 - m)P_B}{100},$$

where m is the molecular percentage of acetone in the mixture and P_A and P_B are the vapour pressures of acetone and methyl ethyl ketone respectively. P' is the observed vapour pressure of the mixture and $\frac{(P-P')}{P'}100$ is the percentage difference.

FIG. 1.

Showing relation between vapour pressure and composition (by weight) of mixtures of acetone and methyl ethyl ketone



Curve I. at 20° | Curve III. at 40°
Curve II. at 30 | Curve IV. at 50

TABLE IV.

Difference between Observed and Calculated Vapour Pressures of Mixtures of Acetone and Methyl Ethyl Ketone at 50°.

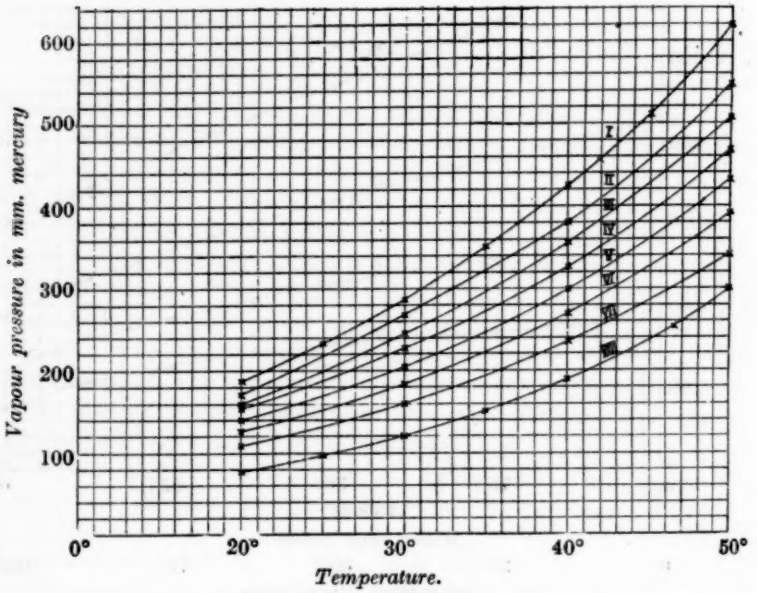
Molecular percentage of acetone = m.	Observed v.p. in mm. of Hg = P'.	Calculated v.p. in mm. of Hg = P.	$\frac{100\,(P-P')}{P'}$.
78·83	548·2	553·0	+0·88
67·42	508·4	516·3	+1·55
55·38	469·7	477·7	+1·70
42·69	230·2	437·0	+1·58
29·27	388·1	393·9	+1·50
15·06	341·9	348·3	+1·87

The maximum deviation is about 1·9 per cent. In Fig. 2, the curves have the familiar shape associated with vapour pressure–temperature curves, and when the logarithms of vapour pressure are plotted against temperature for each mixture and for the pure solvents, the resulting graph is practically a straight line.

There is a considerable difference in the figures given in the

FIG. 2.

Showing relation between temperature and vapour pressure for mixtures of acetone and methyl ethyl ketone.



Curve	I. = Acetone.	Curve	V. = 37½% Acetone (by wt.)
,,	II. = 75% Acetone (by wt.)	,,	VI. = 25 ,, ,, ,,
,,	III. = 62½% ,, ,, ,,	,,	VII. = 12½% ,, ,, ,,
,,	IV. = 50% ,, ,, ,,	,,	VIII. = 100% Methyl ethyl ketone.

literature for the density of acetone. Thus Perkin (T., 1884, **45**, 478) gives D_{15}^{15} 0·79652, which is equivalent to D_4 0·79072.

Linnemann (T., quoted by Perkin) gives D_{15}^{15} 0·7975 or D_4^{20} 0·79170. Perkin's value is considerably lower, and was obtained with acetone purified by the sodium hydrogen sulphite method and boiling at 55·6—55·9°. McElroy and Krug (*J. Soc. Chem. Ind.*, 1893, **12**, 177) give D_4^{20} 0·79197. Squibb (*J. Amer. Chem. Soc.*, 1895, **17**, 200) gives D_{15}^{15} 0·7966 or D_4^{20} 0·7908. This value agrees closely with that obtained by Perkin. Bramley (T., 1916, **109**, 455) obtained

the value D_4^{20} 0·7912. Thus the range of published figures varies from 0·79072 to 0·79197 for the density of acetone at 20°/4°. The result obtained in the present work is the mean of two which agreed exactly, namely, 0·79082. The specific gravities in this work are given to five decimal places, by which is meant that they are correct to four places, the fifth figure being doubtful in each case. It will be seen, therefore, that excellent agreement is obtained with the result of Squibb (D 0·7908) and with that of Perkin (D_4^{20} 0·79072).

The results for the density of acetone at other temperatures agree well with those obtained by Bramley (*loc. cit.*), as shown in the following table.

TABLE V.

Comparison of Results for Density of Acetone at Various Temperatures.

	Density.	
Temperature.	Author.	Bramley.
20°/4°	0·79082	0·7912
30°/4°	0·77931	0·7793
40°/4°	0·76784	0·7674
50°/4°	0·75599	0·7555

The density of methyl ethyl ketone is given by Marshall (T., 1906, **89**, 1376) as 0·81005 at 15°/4°. Extrapolation from the results obtained by the present author gives 0·8101, which agrees very well with Marshall's figure.

The density–concentration curves are all straight lines parallel to each other, thus showing that there is no contraction or expansion in volume on mixing acetone and methyl ethyl ketone at any of the temperatures 20° to 50°.

The density–temperature curves for the pure liquids and for the mixtures are also practically straight lines, the curvature being extremely slight. For acetone, the difference in density per degree over the whole range is 0·001161, and for methyl ethyl ketone it is 0·00106.

Summary.

Vapour pressures and densities of acetone, methyl ethyl ketone, and mixtures of the two have been determined from 20° to 50°.

The vapour pressure–concentration curves all lie between the vapour pressures of the components, there being no sign of a maximum at any point.

The density–concentration curves are straight lines, showing that

no change in volume occurs when acetone and methyl ethyl ketone are mixed in any proportions from 20° to 50°.

In conclusion, the author's best thanks are due to Messrs. Nobel's Explosives Co., Ltd., for whom the work was carried out, and to Mr. Wm. Rintoul, the Manager of the Research Section, for permission to publish the results.

THE RESEARCH LABORATORIES,
ARDEER.

[*Received, July 14th*, 1919.]

XCIX.—*The Constitution of Internal Diazo-oxides (Diazophenols). Part II.*

By GILBERT T. MORGAN and ERIC DODDRELL EVENS.

EARLIER experiments on the nitrated ortho- and para-diazo-oxides of the benzene series showed that 4-nitrobenzene-1-diazo-2-oxide obtained by the diazotisation of 5-nitro-2-aminophenol has the property of forming dihydroxyazo-derivatives which yield metallic lakes having remarkably distinctive colours (Morgan and Porter, T., 1915, **107**, 645).

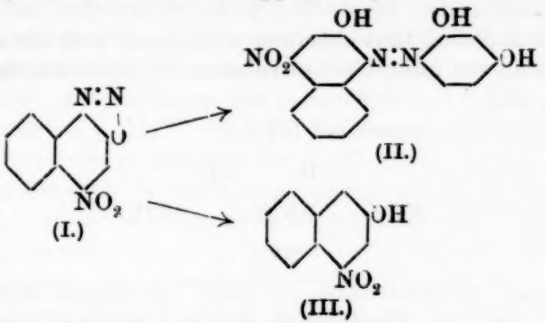
In the present investigation the corresponding diazo-oxide of naphthalene has been examined from this point of view. The results afford an interesting comparison of the differences manifested between benzenoid diazo-oxides and their analogues in the naphthalene series.

4-Nitronaphthalene-1-diazo-2-oxide (I) was first obtained by Friedländer, who passed nitrous fumes into a solution of 2:4-dinitro-α-naphthylamine in moderately concentrated sulphuric acid and added the diazo-solution to alcohol or water (*Ber.*, 1895, **28**, 1951).

The product, which can be prepared in quantitative yield by the methods described in the present paper, has not hitherto been examined in any detail. This very stable internal diazo-oxide couples only with the more reactive phenols, such as resorcinol, phloroglucinol, and 1:3-dihydroxynaphthalene, and in these instances the formation of azo-compounds takes place not only in alkaline solutions but also, and with greater facility, in the presence of strong acids, for example, in glacial acetic acid containing concentrated mineral acid.

4-*Nitro*-β-*naphthol*-1-*azoresorcinol* (II) functions as an acid mordant dye giving reddish-brown shades on wool which are changed

into lakes of characteristic colour by the action of metallic mordants (chromium, vanadium, copper, etc.):



On prolonged boiling with ethyl alcohol either alone or in the presence of a metallic catalyst, 4-nitronaphthalene-1-diazo-2-oxide loses its diazo-group and becomes converted into 4-*nitro*-β-*naphthol* (III), the fourth isomeride to be discovered of the seven possible nitro-β-naphthols.

4-Nitro-β-naphthol is less reactive than β-naphthol. It is much less easily alkylated, and couples more slowly with azo-compounds. The 4-nitro-1-azo-β-naphthols, from benzenediazonium chloride and *p*-nitrobenzenediazonium chloride, are insoluble in aqueous alkali hydroxides, in this respect resembling the azo-β-naphthols, the insolubility of which in aqueous alkalis is a matter of so much theoretical interest and industrial importance. The azo-dyes obtained from 4-nitro-β-naphthol differ considerably in colour from those derived from β-naphthol.

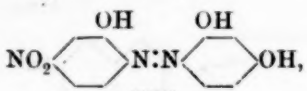
The diazotisation of 2:4-dinitroaniline in concentrated sulphuric acid has already been effected, and the results indicate that the nitro-group is less readily removed than in the foregoing case of 2:4-dinitronaphthalene-1-diazonium sulphate. The elimination of a nitro-group from 2:4-dinitrobenzene-1-diazonium sulphate is not effected merely by dilution with water. In this instance it is necessary to neutralise the solution with alkali carbonate (Badische Anilin- & Soda-Fabrik, D.R.-P., 144640), when a soluble form of 5-nitro-2-diazophenol is produced. Repetition of this experiment showed that the formation of this ortho-diazophenol is not quantitative. An insoluble product is obtained, the amount of which varies from 14 to 20 per cent. of the 2:4-dinitroaniline employed. This by-product, which is still under examination, is an ill-defined substance having the properties of an external diazo-oxide. It couples readily with either alkaline β-naphthol or β-naphthylamine in acetic acid solution.

The soluble variety of 5-nitro-2-diazophenol contained in the

clear, yellow filtrate from the foregoing insoluble product couples with aromatic *m*-diamines, phenols, naphthols, aminonaphthols, and their sulphonic acids.

The azo-β-naphthol thus obtained is identical with the compound produced from the insoluble 4-nitrobenzene-1-diazo-2-oxide (M. and P., T., *loc. cit.*).

5-*Nitrophenol*-2-*azoresorcinol* (IV),



(IV.)

gives intensely coloured lakes on wool mordanted with metallic hydroxides. Similar dihydroxyazo-dyes are obtained from chromotropic acid and from aminonaphtholsulphonic acids coupled in alkaline solution. These colouring matters are extremely sensitive to metals, and are converted into green, purple, and blue lakes by the action of metallic mordants.

Summary.

1. 2:4-Dinitronaphthalene-1-diazonium sulphate is unstable in dilute acid and passes quantitatively into the sparingly soluble 4-nitronaphthalene-1-diazo-2-oxide, a very stable diazo-oxide yielding azo-derivatives only with difficulty.

2. 4-Nitronaphthalene-1-diazo-2-oxide undergoes loss of the diazo-group with the production of 4-nitro-β-naphthol.

3. 2:4-Dinitrobenzene-1-diazonium sulphate is stable in dilute acid, but in neutral or slightly alkaline solution it yields the soluble 5-nitro-2-diazophenol together with an insoluble by-product. This soluble diazo-compound furnishes *o*-dihydroxyazo- and *o*-aminohydroxyazo-dyes, giving intensely coloured lakes with metallic mordants.

Experimental.

I. Diazotisation of 2:4-*Dinitro*-α-*naphthylamine Sulphate.*

2:4-Dinitro-α-naphthylamine, the starting point of this part of the investigation, was obtained in three different ways.

1. *Preparation from* 2:4-*Dinitro*-α-*naphthol.*—Finely powdered α-naphthol (50 grams) was added to 100 c.c. of concentrated sulphuric acid and the mixture stirred until a clear solution was obtained. On heating this liquid on the water-bath for fifteen minutes, α-naphtholdisulphonic acid separated when the mixture

was cooled, and the solidified mass was dissolved in 250 c.c. of water. The cooled solution was added slowly to 60 c.c. of nitric acid (D 1·42), the temperature being maintained below 10°. The nitration mixture was then slowly warmed to 100° and maintained at this temperature for fifteen minutes, the pasty mass being stirred continuously. After cooling, the pale yellow 2:4-dinitro-α-naphthol was collected (m. p. 132°; yield, 83 per cent.).

The authors are indebted to Dr. L. G. Paul for this process, in which the nitration is much more under control than when the nitric acid is added to solutions of α-naphtholdisulphonic acid. Prolonged sulphonation on the water-bath led to α-naphtholtrisulphonic acid with subsequent formation of naphthol yellow S.

Dinitro-α-naphthol (60 grams) and 700 c.c. of alcoholic ammonia saturated at 0° were heated for ten hours at 195—200° in a rotating steel autoclave, the pressure attained being 39 kilos. per square cm. 2:4-Dinitro-α-naphthylamine (40 grams) separated from the alcoholic solution on cooling; the filtrate contained the ammonium salt of 2:4-dinitro-α-naphthol together with tarry impurities. When crystallised from glacial acetic acid, 2:4-dinitro-α-naphthylamine melted at 239°. Concentrated aqueous ammonia, under the foregoing conditions, did not affect dinitro-α-naphthol.

2. *Preparation from Aceto-α-naphthalide* (compare Meldola, *Ber.*, 1886, **19**, 2683).—Aceto-α-naphthalide (100 grams) was dissolved in 200 c.c. of glacial acetic acid and nitrated with 52 c.c. of nitric acid (D 1·52) mixed with an equal volume of glacial acetic acid. During the addition of the mixed acids, the temperature was kept below 70° and subsequently raised to 96° until the dinitro-compound began to separate. The mixture was then cooled and the separating solid crystallised from glacial acetic acid (yield, 52 per cent.). Twenty grams of purified 2:4-dinitroaceto-α-naphthalide were added to a cold mixture of 30 c.c. of water and 200 c.c. of concentrated sulphuric acid. The mixture was warmed at 60—70° for a few minutes, allowed to cool for fifteen minutes, and poured into 400 c.c. of ice-water, when 2:4-dinitro-α-naphthylamine was precipitated.

3. *Preparation from Toluene-*p*-sulphon-α-naphthylamide.*—Toluene-*p*-sulphon-α-naphthylamide, prepared by triturating together α-naphthylamine, toluene-*p*-sulphonyl chloride, and anhydrous sodium acetate in molecular proportions, was washed with warm water rendered alkaline with sodium carbonate and crystallised from alcohol (yield, 96 per cent.). Fifty grams of this preparation were dissolved in 400 c.c. of hot glacial acetic acid. The solution when cooled to 45° deposited crystals of the dissolved substance, and the mixture was nitrated with 30 c.c. of nitric acid

(D 1·42) mixed with 30 c.c. of glacial acetic acid. The temperature rose to 60° and the mixture was subsequently heated to 80° for one hour. On cooling, *toluene*-p-*sulphon*-2:4-*dinitro*-α-*naphthylamide* crystallised, and a further crop was obtained on diluting with water. When crystallised from alcohol this compound separated in radiating clusters of pale yellow, silky needles melting at 165—166° (yield, 80 per cent.):

0·3614 gave 36·3 c.c. N_2 at 22° and 763·6 mm. N = 11·42.

$C_{17}H_{13}O_6N_3S$ requires N = 10·85 per cent.

This dinitro-compound was hydrolysed by adding 20 grams to a cooled mixture of 200 c.c. of concentrated sulphuric acid and 30 c.c. of water, and warming at 70° for ten minutes. On adding the cooled mixture to ice-cold water, 2:4-dinitro-α-naphthylamine was precipitated, the yield being quantitative.

4-Nitronaphthalene-1-diazo-2-oxide (I).

2:4-Dinitro-α-naphthylamine (3 grams) was dissolved in 30 c.c. of cold concentrated sulphuric acid, 5·5 grams of nitrosyl sulphate were added, and the solution was diluted with fragments of ice until on further dilution of a portion with water a clear solution was obtained. The main solution of diazotised amine was then poured into 800 c.c. of water and left for one hour, when the precipitated diazo-oxide was collected and crystallised from light petroleum (b. p. 60—80°). This product, which separated in yellow needles, decomposed with intumescence at 130—134°.

The foregoing diazotisation was also effected with dry sodium nitrite dissolved in concentrated sulphuric acid at temperatures below 70°, the solution being cooled before use. Moreover, the diazo-oxide was prepared from the acyl derivatives of 2:4-dinitro-α-naphthylamine without isolating the base itself.

2:4-Dinitroaceto-α-naphthalide (30 grams) or the corresponding amount of toluene-*p*-sulphon-2:4-dinitro-α-naphthylamide added to 300 c.c. of concentrated sulphuric acid diluted with 42 c.c. of water underwent hydrolysis on warming to 70°. After cooling to 0° the solution was treated with 10 grams of sodium nitrite dissolved in 30 c.c. of concentrated sulphuric acid. Fragments of ice were added until a test portion on further dilution with water gave no precipitate of undiazotised amine. The solution was then poured into 1 litre of ice-water. A clear solution was produced, which after thirty seconds became cloudy and deposited a crystalline, brownish-yellow precipitate of the diazo-oxide (yield, 92 per cent.).

4-Nitronaphthalene-1-diazo-2-oxide was very sparingly soluble in water; it dissolved readily in benzene, acetone, or acetic acid, and

crystallised from these solvents. It was moderately soluble in alcohol, and on adding sodium hydroxide to this solution nitrogen was evolved and acetaldehyde produced.

With resorcinol, phloroglucinol, or 1:3-dihydroxynaphthalene the diazo-oxide reacted in alcoholic solution on the addition of a drop of aqueous sodium hydroxide, giving a blue coloration which can be used as a test for this diazo-derivative.

4-Nitronaphthalene-1-diazo-2-oxide has the remarkable property of coupling to form azo-compounds with the foregoing polyhydric phenols in a mixture of concentrated hydrochloric and acetic acids. It is, however, only with these very reactive phenols that this diazo-oxide has been found to combine.

4-Nitro-β-naphthol-1-azoresorcinol (II).

Five grams of 4-nitronaphthalene-1-diazo-2-oxide and 2·5 grams of resorcinol were dissolved in 50 c.c. of glacial acetic acid to which 5 c.c. of concentrated hydrochloric acid were added. After two days about 1 gram of the hydroxyazo-compound had separated, and on concentrating the filtrate a further 0·5 gram was obtained.

On pouring the filtrate into water, 5 grams of somewhat tarry azo-compound separated. The crystalline portions were crystallised repeatedly from glacial acetic acid, when the compound separated in reddish-black, nodular crystals melting at 254—256°:

0·1942 gave 20·25 c.c. N_2 at 18° and 762 mm. N = 12·13.

$C_{16}H_{11}O_5N_3$ requires N = 12·92 per cent.

4-Nitro-β-naphthol-1-azoresorcinol gave indigo-blue alkali salts in aqueous alkali hydroxides and developed an intense violet coloration with concentrated sulphuric acid. Although only sparingly soluble in water, this hydroxyazo-compound can be employed as an acid mordant dye. On unmordanted wool it furnished reddish-brown shades, becoming violet on subsequent treatment with copper sulphate and acetic acid. On chromium mordanted wool a bluish-black lake was produced. 4-Nitronaphthalene-1-diazo-2-oxide when coupled with phloroglucinol or 1:3-dihydroxynaphthalene in the presence of glacial acetic acid and concentrated hydrochloric acid gave rise to similar hydroxyazo-compounds dyeing chrome-mordanted wool in bluish-violet shades. Like the preceding substance these hydroxyazo-derivatives dissolved readily in the ordinary organic solvents, but showed very little tendency to crystallise. They gave rise to blue alkali salts and developed violet colorations with concentrated sulphuric acid.

4-Nitro-β-naphthol (III).

4-Nitronaphthalene-1-diazo-2-oxide (40 grams) was heated in a reflux apparatus with 600 c.c. of alcohol and 12 grams of finely divided copper for twelve hours. Acetaldehyde was evolved, and at the end of this period a drop of the solution tested with alkaline resorcinol no longer gave a blue coloration. This negative result indicated the absence of unaltered diazo-oxide, whereas the production of a red azo-dye with diazotised sulphanilic acid revealed the presence of a phenolic compound.

The filtered solution was evaporated to remove alcohol, and the residue extracted repeatedly with hot water. On cooling, the aqueous extracts furnished yellow, felted needles of 4-nitro-β-naphthol (yield about 38 per cent. of the theoretical). The copper precipitate contained an intensely coloured organic compound insoluble in alcohol, but dissolving in pyridine or aniline to a deep blue solution and in nitrobenzene to a purple solution. This product, owing to its insoluble, uncrystallisable nature, was not examined further.

Many experiments were carried out on the preparation of 4-nitro-β-naphthol, and it was found that other metals gave better results than copper in the reduction of the diazo-oxide.

With zinc dust (8 grams) and the foregoing proportions of diazo-oxide and alcohol the reduction was complete after boiling for sixteen hours, the yield of recrystallised 4-nitro-β-naphthol being 45 per cent. of the theoretical. The optimum result was obtained with powdered aluminium (7 grams) added to 70 grams of the diazo-oxide suspended in 1050 c.c. of alcohol. This mixture when heated under reflux for thirty-two hours gave a negative test with alkaline resorcinol, and after distilling off the alcohol and acetaldehyde and extracting the residue with hot water a yield of 58—64 per cent. of 4-nitro-β-naphthol was obtained.

This decomposition was effected in twenty-six hours by heating at 50° the diazo-oxide (64 grams) suspended in alcohol (1000 c.c.) with 24 c.c. of 30 per cent. hypophosphorous acid, the yield of 4-nitro-β-naphthol being 53 per cent.

In ethyl alcohol alone without metallic catalysts a yield of 45 per cent. of 4-nitro-β-naphthol was obtained after twenty-four hours' boiling. The replacement of ethyl by butyl alcohol lowered the yield considerably, as also did the employment of formic acid and copper powder.

After repeated crystallisation from carbon tetrachloride or benzene, 4-nitro-β-naphthol melted at 120°:

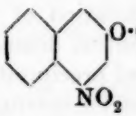
0·1810 gave 12 c.c. N_2 at 25° and 768 mm. N = 7·48.
$C_{10}H_7O_3N$ requires N = 7·41 per cent.

4-Nitro-β-naphthol crystallised from light petroleum (b. p. 80—100°), hot water, or carbon tetrachloride in slender, yellow needles, and from benzene in compact, tabular prisms. It dissolved in aqueous alkali hydroxides to deep red solutions. Its potassium salt crystallised in glistening, red needles, but was hydrolysed on continued washing with water.

When reduced with tin and hydrochloric acid or with zinc dust and ammonium chloride in 50 per cent. alcohol, 4-nitro-β-naphthol was reduced to 4-amino-β-naphthol, but prolonged digestion on the water-bath with these reducing agents led to the elimination of the amino-group and the formation of 1 : 3-dihydroxynaphthalene (compare Friedländer, *Ber.*, 1895, **28**, 1952).

Attempts to convert 4-nitro-β-naphthol into 4-nitro-β-naphthylamine by heating under pressure with aqueous or alcoholic ammonia were not successful. It was not found possible to obtain a nitro-derivative of Meldola's blue by condensing 4-nitro-β-naphthol with *p*-nitrosodimethylaniline hydrochloride in alcohol or acetic acid.

Experiments on alkylation showed that 4-nitro-β-naphthol was much less reactive than β-naphthol. Boiling for twelve hours with alcohol containing 2 per cent. of sulphuric acid did not lead to ethylation of the nitro-compound.

4-Nitro-β-naphthyl Methyl Ether, 

The sodium salt of 4-nitro-β-naphthol was suspended in dry xylene (10 parts) and boiled for eight hours with a slight excess of methyl sulphate. The solvent was evaporated, and the residue crystallised repeatedly from a mixture of benzene and alcohol:

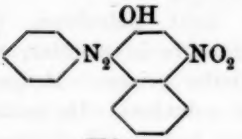
0·2227 gave 13·8 c.c. N_2 at 24° and 760 mm. N = 6·92.
$C_{11}H_9O_3N$ requires N = 6·90 per cent.

4-Nitro-β-naphthyl methyl ether crystallised from a mixture of benzene and alcohol in lustrous, brown needles melting at 100—103°.

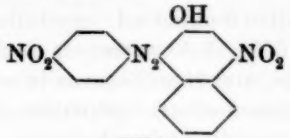
Azo-derivatives of 4-Nitro-β-naphthol.

4-Nitro-β-naphthol when dissolved in aqueous alkali hydroxides or carbonates coupled readily with various diazonium compounds.

Benzene-1-*azo*-4-*nitro*-β-*naphthol* (V),



(V.)



(VI.)

A solution of benzenediazonium chloride added to 4-nitro-β-naphthol (1 mol.) dissolved in *N*/2-sodium hydroxide gave at once an insoluble, dark red azo-compound which, after crystallisation from benzene, separated in dark brownish-red needles melting at 206—207°:

0·2088 gave 27·6 N_2 at 22° and 761·5 mm. N = 14·98.

$C_{16}H_{11}O_3N_3$ requires N = 14·33 per cent.

Benzene-1-azo-4-nitro-β-naphthol dissolved only sparingly in alcohol; it was insoluble in aqueous sodium hydroxide, in this respect resembling benzeneazo-β-naphthol. The nitro-group had not rendered the compound acidic. Concentrated sulphuric acid developed a magenta coloration, whilst alcoholic sodium hydroxide gave a deep red solution.

p-*Nitrobenzene*-1-*azo*-4-*nitro*-β-*naphthol* (VI).

A dilute solution of *p*-nitrobenzenediazonium chloride added to 4-nitro-β-naphthol dissolved in excess of *N*/2-sodium hydroxide gave a purplish-red precipitate of the azo-derivative difficult to crystallise on account of its sparing solubility in the ordinary solvents. From glacial acetic acid the azo-compound separated in nodular crystals melting at 231°:

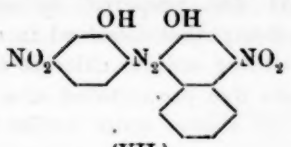
0·1691 gave 23·5 c.c. N_2 at 17° and 767·4 mm. N = 16·29.

$C_{16}H_{10}O_5N_4$ requires N = 16·57 per cent.

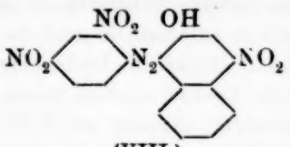
p-Nitrobenzene-1-azo-4-nitro-β-naphthol, which was insoluble in aqueous alkali hydroxides, dissolved in alcoholic sodium hydroxide to an intense purplish-blue solution probably containing a quinonoid sodium salt, hydrolysed by water with the regeneration of the original azo-compound. Concentrated sulphuric acid and this azo-compound developed a purple coloration.

When developed on calico padded with alkaline 4-nitro-β-naphthol and Turkey red oil this azo-compound gave a crimson-red colour quite distinct from paranitroaniline-red. In this case deeper and more even shades were obtained when the 4-nitro-β-naphthol was dissolved in aqueous sodium carbonate rather than in sodium hydroxide solution.

Azo-4-nitro-β-naphthols from 2:4-Dinitroaniline,



(VII.)



(VIII.)

2:4-Dinitroaniline (3 grams) dissolved in cold concentrated sulphuric acid was diazotised as described on p. 1136, and the dilute acid solution of 2:4-dinitrobenzenediazonium sulphate added to a cold solution of 4-nitro-β-naphthol (1 mol.) dissolved in excess of normal sodium hydroxide. A dark reddish-brown precipitate *A* (3 grams) was at once produced, and the filtrate from this substance gave on acidification a paler red precipitate *B* (2 grams).

The former precipitate, *A*, which was probably a sodium salt, was boiled with glacial acetic acid to set free the azo-compound, which was then crystallised from anisole. The product separated in dark brownish-red, nodular crystals melting very indefinitely at 132—166°:

0·0738 gave 10·35 c.c. N_2 at 26° and 764 mm. N = 15·64.
$C_{11}H_{10}O_6N_4$ requires N = 15·82 per cent.

This analytical result corresponds with formula VII for a dihydroxyazo-compound which was probably precipitated in the form of its sparingly soluble sodium salt.

The second precipitate *B* also crystallised from anisole in dark red, tabular crystals with a green reflex. This product, when boiled with alcohol to remove the solvent, melted indefinitely between 200° and 250°:

0·2020 gave 31·7 c.c. N_2 at 19° and 762·4 mm. N = 18·09.
$C_{16}H_9O_7N_5$ requires N = 18·28 per cent.

This result corresponds with formula VIII for an azo-compound containing three nitro-groups. This azo-4-nitro-β-naphthol containing three nitro-groups is apparently acidic and remained dissolved until the alkaline solution was acidified. The two products of this azo-coupling were not very crystallisable, but the analytical data showed that the separation by means of alkali was practically complete.

With concentrated sulphuric acid, compound *A* (VII) gave a purple coloration, whereas compound *B* (VIII) developed an indigo-blue coloration.

Azo-colouring Matters from 4-Nitro-β-naphthol.

The 4-nitro-derivative of orange II was prepared by adding diazotised sulphanilic acid to 4-nitro-β-naphthol dissolved in excess of cold *N*/2-sodium hydroxide. On adding sodium chloride to the solution heated on the water-bath, the dye precipitated as a dark red powder, dyeing wool in deep red shades quite unlike those obtained from orange II.

p-Nitroaniline-*o*-sulphonic acid diazotised and coupled with alkaline 4-nitro-β-naphthol gave an acid azo-dye furnishing orange shades on wool.

Picramic acid diazotised and coupled with 4-nitro-β-naphthol furnished a dye melting above 250° and giving reddish-brown shades on unchromed wool, the chrome lake being brownish-purple. The three foregoing dyes gave deep red colorations with concentrated sulphuric acid.

Calico padded with 4-nitro-β-naphthol, aqueous sodium carbonate, and Turkey-red oil was passed through a solution of sodium acetate and the bisdiazonium chloride from dianisidine. The fabric was dyed in dark blue shades.

Primuline dyed and diazotised on cotton gave with alkaline 4-nitro-β-naphthol a purple maroon colour, quite unlike the red ingrain dye from β-naphthol.

Direct cotton colours dyeing in purple shades were obtained by coupling alkaline 4-nitro-β-naphthol with the diazo-derivatives of safranine and 4:4′-diaminostilbene-2:2′-disulphonic acid.

II. Diazotisation of 2:4-Dinitroaniline Sulphate.

The 2:4-dinitroaniline employed in these experiments was obtained in practically quantitative yield by heating 4-chloro-1:3-dinitrobenzene with nine parts by weight of concentrated aqueous ammonia at 110° for two hours in the rotating autoclave.

In the following experiments, 2:4-dinitroaniline was diazotised in concentrated sulphuric acid. Dry sodium nitrite (2·2 grams) was added to 7·5 c.c. of cold concentrated sulphuric acid, and the mixture heated to 75°. The clear liquid thus obtained was cooled in ice, and 5 grams of 2:4-dinitroaniline were added with stirring. After two hours, the pasty mass was diluted to 700 c.c. with ice and water. The solution at this stage contained 2:4-dinitrobenzenediazonium sulphate, as was proved by adding the liquid slowly to alkaline β-naphthol, when 2:4-dinitrobenzeneazo-β-naphthol was deposited as a bright orange-red precipitate very sparingly soluble in the ordinary organic media. This product

crystallised from hot glacial acetic acid in orange-red needles, and did not melt below 270°. With cold concentrated sulphuric acid it developed a purple-blue coloration, and with alcoholic sodium hydroxide a deep blue solution.

5-Nitro-2-diazophenol.

Elimination of the ortho-nitro-group in 2:4-dinitrobenzenediazonium sulphate was effected by pouring the diazo-solution, prepared as in the foregoing diazotisation, into a litre of water containing 17·4 grams of sodium carbonate and 400 grams of ice. After one hour, a yellow precipitate was collected which, on drying at the ordinary temperature, weighed 0·7 gram. The insoluble product, which melted and decomposed between 64° and 80°, coupled with alkaline β-naphthol, yielding a purplish-brown azo-compound. When half the amount of water was used in the neutralisation, the amount of this by-product increased to 0·9 gram.

The yellow, alkaline solution from this by-product was added to excess of alkaline β-naphthol, when the yellow colour of the 5-nitrodiazophenol disappeared, and a deep blue precipitate with bronze reflex was produced, the supernatant liquid having a brown tint. This blue compound was a sparingly soluble sodium salt which, on treatment with alcoholic hydrogen chloride, yielded a purplish-red azo-β-naphthol melting at 228°, and identical with the 4-nitro-2-hydroxybenzeneazo-β-naphthol obtained from the internal diazo-oxide of 5-nitro-2-aminophenol (T., 1915, **107**, 655). The identity of the two compounds was confirmed by a mixed melting-point determination and by the formation of the characteristic metallic lakes from the foregoing preparation.

The production of a dihydroxyazo-compound from β-naphthol and the alkaline solution of the diazo-derivative of 2:4-dinitroaniline showed that in alkaline solution the ortho-nitro-group had been replaced by hydroxyl. This conclusion was confirmed by the following experiments.

5-Nitrophenol-2-resorcinol (IV).

Sodium nitrite (1·1 grams) was added to 3·75 c.c. of concentrated sulphuric acid, the temperature being kept below 70°. The warm solution was cooled, and 2·5 grams of 2:4-dinitroaniline were added. After one hour, the brown paste was added to a solution of 8·8 grams of sodium carbonate in 300 c.c. of water containing 100 grams of ice.

The yellow solution filtered from the insoluble by-product (0·4

gram) was treated with 1·5 grams of resorcinol in 5·7 c.c. of 20 per cent. aqueous sodium hydroxide. The intense purplish-red alkaline solution was subsequently warmed on the water-bath, and the sodium salt of the azo-dye precipitated by the addition of 100 grams of sodium chloride. This sodium salt (4·5 grams) gave the orange-red azo-resorcinol on treatment with dilute sulphuric acid. When crystallised from glacial acetic acid, it separated in small, reddish-brown needles decomposing at 225°. The sulphuric acid coloration was deep red:

0·0997 gave 13·75 c.c. N_2 at 21·5° and 762 mm. N = 15·67.

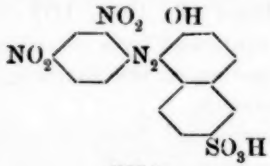
$C_{12}H_9O_5N_3$ requires N = 15·27 per cent.

The percentage of nitrogen required for dinitrobenzeneazo-resorcinol is 18·42.

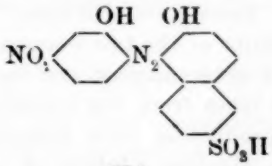
On unchromed wool, this azo-resorcinol gave bright orange-red shades, changing to deep claret on chroming subsequently with 1 per cent. of chromic acid. By the metachrome process of dyeing, very deep purple shades were produced, appearing almost black.

The marked alteration of shade produced by mordanting with chromium suggested the arrangement of two hydroxyl groups contiguous to the azo-group, as indicated in the above formula. Further evidence was obtained by a comparative experiment made on β-naphthol-6-sulphonic acid.

Azo-dyes from 2:4-Dinitroaniline and Schäffer's Acid.



(IX.)



(X.)

(1) 2:4-Dinitroaniline (2·5 grams) was added to a solution of 1·1 grams of sodium nitrite in 7·5 c.c. of concentrated sulphuric acid, and the resulting paste added to 150 c.c. of cold water. This acid solution of 2:4-dinitrobenzenediazonium sulphate was added to 3·5 grams of Schäffer's salt dissolved in 100 c.c. of water and 70 c.c. of 5*N*-sodium hydroxide. After one hour, the solution was heated on the water-bath and the azo-dye precipitated with 50 grams of salt. This dye, 2:4-dinitrobenzeneazo-β-naphthol-6-sulphonic acid (IX), gave orange shades on unmordanted wool not altered by chroming.

(2) 2:4-Dinitroaniline (2·5 grams) was diazotised as before in concentrated sulphuric acid; the diluted diazo-solution was

rendered alkaline with excess of aqueous sodium carbonate and added to an alkaline solution of Schäffer's salt. After one hour, the solution was warmed and the dye precipitated with sodium chloride. This dye, 4-nitro-2-hydroxybenzeneazo-β-naphthol-6-sulphonic acid (X), gave reddish-brown shades on wool, changing to deep violet on chroming.

(3) The dinitroaniline (2·5 grams) was diazotised as before, and to the dilute acid solution was added 3·4 grams of copper sulphate; the liquid was then rendered alkaline with sodium carbonate and added to an alkaline solution of Schäffer's salt. Coupling occurred slowly, and was completed by warming, the dye being then salted out. It gave purple shades on wool, which were not affected by after-chroming. These purple shades were reproduced by treating the dyed patterns of the second preparation with copper sulphate. Similar purple shades were obtained by treating the dihydroxyazo-dye (X) with cobalt chloride or chlorocobaltipentammine chloride, $[ClCo(NH_3)_5]Cl_2$.

These experiments point conclusively to the formation of a soluble form of 5-nitro-2-diazophenol when an acid solution of 2:4-dinitrobenzenediazonium sulphate is rendered alkaline with sodium carbonate.

The azo-dyes produced by coupling this alkaline diazo-solution with various phenolic derivatives and reactive amines all have the property of forming distinctly coloured metallic lakes. With 2:4-tolylenediamine, the aminohydroxyazo-dye was produced in dilute acetic acid. In the case of the aminonaphtholsulphonic acids, the coupling was effected in the presence of sodium hydroxide. With chromotropic acid, the most favourable result was obtained on using milk of lime as the alkali.

Azo-dyes from 5-Nitro-2-diazophenol.

Coupling substance.	Colour of dye on unmordanted wool.	Colour of mordanted dye.
2:4-Tolylenediamine.	—	Metachrome process: purplish-black lake (1 per cent.).
2-Hydroxy-3-naphthoic acid.	Reddish-brown.	Purple chromium lake.
1:8-Dihydroxynaphthalene-3:6-disulphonic acid (chromotropic acid).	Bluish-red.	Chromium—greenish-blue. Vanadium—blue. Copper—bluish-purple. Cobalt—purplish-blue.
8-Amino-α-naphthol-3:6-disulphonic acid (H acid).	Purple.	Chromium—dark green. Vanadium—green. Copper—intense blue. Cobalt—dark bluish-purple.

Azo-dyes from 5-Nitro-2-diazophenol (continued).

Coupling substance.	Colour of dye on unmordanted wool.	Colour of mordanted dye.
8 - Amino - α - naphthol - 5-sulphonic acid (S acid).	Mauve.	Chromium—sage-green. Vanadium—bright green. Copper—bright blue. Cobalt—blue. Nickel—blue. Iron—dull violet. Manganese—dull violet. Uranium—dark lavender blue.
7 - Amino - α - naphthol - 3-sulphonic acid (J acid).	Crimson-red.	Chromium—dark bluish-grey. Vanadium—dark purplish-blue. Copper—purple. Cobalt—maroon. Uranium—maroon.

The foregoing azo-colouring matters when dyed on unmordanted wool are extremely sensitive to metals, this property being due, undoubtedly, to the ease with which the metallic lakes are produced.

The authors desire to express their thanks to the Research Grant Committees of the Royal Society and Chemical Society for grants which have partly defrayed the expenses of this investigation.

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C.—*β-Naphthylmethylamine.*

By GILBERT T. MORGAN and FREDERICK PAGE EVENS.

β-NAPHTHYLMETHYLAMINE, the simplest alkyl derivative of β-naphthylamine, has not hitherto received detailed attention, probably owing to the circumstance that it is not produced readily by the action of ordinary methylating agents on the primary base.

Powerful methylating agents, such as methyl iodide in excess, lead to quaternary ammonium salts, from which the quaternary ammonium hydroxide and β-naphthyldimethylamine are successively obtained (Hantzsch, *Ber.*, 1880, **13**, 2054; Bamberger, *ibid.*, 1889,

22, 1306). By operating with equal weights of β-naphthylamine and methyl iodide at 100° in methyl-alcoholic solution, von Pechmann and Heinze produced a certain proportion of β-naphthylmethylamine, which, however, required purification by conversion into its nitrosoamine and subsequent reduction, so that the yield of recovered base was not satisfactory (*Ber.*, 1895, **28**, 2370; 1897, **30**, 1785). Pschorr and Karo subsequently obtained the base by the action of methyl sulphate on benzenesulphon-β-naphthalide and subsequent hydrolysis of the product (*Ber.*, 1906, **39**, 3142).

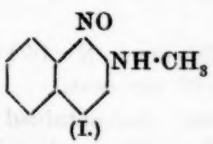
It has now been found that β-naphthylmethylamine can be prepared in excellent yield and in a state of purity by the interaction of β-naphthol and aqueous methylamine at high temperatures under pressure.

$$C_{10}H_7{\cdot}OH + NH_2{\cdot}CH_3,HCl + NaOH = C_{10}H_7{\cdot}NH{\cdot}CH_3 + NaCl + 2H_2O.$$

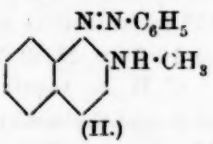
β-Naphthol (100 grams), methylamine hydrochloride (75 grams), and 190 c.c. of 5*N*-sodium hydroxide were heated in a rotating steel autoclave at 200—220° for seven hours, the pressure attained being about 21 kilos. per sq. cm. The oily contents of the autoclave were extracted successively with aqueous sodium hydroxide to remove unaltered β-naphthol, and with benzene to dissolve β-naphthylmethylamine. The benzene extract, after drying over calcium chloride, was distilled first under the ordinary and then under diminished pressure, the yield of secondary base being upwards of 80 per cent. of the theoretical.

β-Naphthylmethylamine boiled at 317°/766 mm. and at 207°/60 mm., and when freshly distilled was colourless, but darkened rapidly on exposure to the air. It was identified by its solid nitrosoamine, which crystallised in pale yellow needles and melted at 88° (Pechmann gives 90°; Pschorr and Karo, 88—89°).

1-*Nitroso-β-naphthylmethylamine* (I).



(I.)



(II.)

β-Naphthylmethylnitrosoamine (5 grams) was suspended in 20 c.c. of alcohol, and 20 c.c. of saturated alcoholic hydrogen chloride were slowly added with vigorous stirring at 0°. The nitrosoamine partly dissolved and the solution darkened. After twenty hours, a few dark green crystals had separated, and the mixture was poured into water. The hydrochloride of the nitroso-

base dissolved, whereas unaltered nitrosoamine was precipitated. On adding aqueous ammonia to the filtrate, the nitroso-base separated, and was crystallised from acetone, when it was obtained in dark green plates melting at 142°:

0·1041 gave 13·5 c.c. N_2* at 17° and 753 mm. N = 14·95.

$C_{11}H_{10}ON_2$ requires N = 15·05 per cent.

The optimum yield of 1-*nitroso-β-naphthylmethylamine* obtained by the foregoing process was 75 per cent. of the theoretical. Unlike β-naphthylmethylnitrosoamine, this nitroso-base gave no Liebermann reaction. The conversion of 1-nitroso-β-naphthylmethylamine into the anhydro-base (methenyl-1:2-naphthylenediamine), $C_{10}H_6\langle^{N}_{NH}\rangle CH$, did not proceed smoothly by the method of O. Fischer and Hepp, employed in the case of the ethenyl analogue (*Ber.*, 1887, **20**, 2471), but when the nitroso-base was heated in alcoholic hydrogen chloride at 100° in a sealed tube, the hydrochloride of the anhydro-base separated in reddish-white crystals.

Azo-derivatives of β-Naphthylmethylamine.

The azo-derivatives of β-naphthylmethylamine were prepared by two general methods, namely, (1) interaction of the base and diazonium salts, and (2) condensation of β-naphthylmethylnitrosoamine with primary aromatic amines.

Benzeneazo-β-naphthylmethylamine (II).

The diazonium chloride from 1 gram of aniline was added in aqueous solution to β-naphthylmethylamine (1·7 grams) dissolved in cold dilute hydrochloric acid; a crimson coloration developed, and the addition of sodium acetate induced coagulation of the azo-compound. The viscid precipitate was dissolved in hot alcohol, from which the product crystallised in felted, scarlet needles melting at 82—83° (quantitative yield):

0·1176 gave 16·6 c.c. N_2 at 18° and 750 mm. N = 16·14.

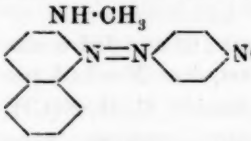
$C_{17}H_{15}N_3$ requires N = 16·09 per cent.

Benzeneazo-β-naphthylmethylamine was also obtained in satisfactory yield on warming a glacial acetic acid solution of β-naphthylmethylnitrosoamine and aniline in molecular proportions.

The product, which was precipitated on diluting the acetic acid solution with water, was identical with the foregoing preparation.

* In this and the following nitrogen estimations the gas was measured over 33 per cent. aqueous potassium hydroxide.

p-*Nitrobenzene*-1-*azo*-β-*naphthylmethylamine*,



An acid solution of *p*-nitrobenzenediazonium chloride (1 mol.) was added to β-naphthylmethylamine (1 mol.) dissolved in dilute hydrochloric acid, the temperature being below 6°. Sodium acetate precipitated the azo-compound in quantitative yield. The reddish-brown product was crystallised from ethyl acetate, acetone, benzene, or glacial acetic acid; it separated in matted, dark brown needles with bronze reflex, and melted at 190—192°:

0·0977 gave 15·1 c.c. N_2 at 15·5° and 750 mm. N = 17·85.

$C_{17}H_{14}O_2N_4$ requires N = 18·30 per cent.

p-Nitrobenzeneazo-β-naphthylmethylamine was also produced by warming together in glacial acetic acid molecular proportions of *p*-nitroaniline and β-naphthylmethylnitrosoamine.

Like the preceding compound, this azo-derivative developed an intense violet coloration with concentrated sulphuric acid.

Azo-dyes from β-Naphthylmethylamine.

These azo-colouring matters can be obtained by the two general methods outlined in the foregoing preparations.

Diazo-derivative of amino-acid.	Tinctorial properties of the resulting dye.	Coloration in concentrated sulphuric acid.
1. Sulphanilic acid.	Scarlet on wool.	Reddish-blue.
2. Naphthionic acid.	Dark red on wool.	Dark violet.
3. Picramic acid:		
Direct dye.	Dull purple on wool.	Reddish-brown.
Dyed by metachrome process.	After prolonged boiling (8 hours) a dark purple unlike the analogous dye from β-naphthylamine, which changes to olive-green shades.	
4. Diaminostilbenedisulphonic acid.	Purple on unmordanted cotton much bluer in shade than Hessian Purple N. from β-naphthylamine.	Greenish-blue.

Acyl Derivatives of β-Naphthylmethylamine.

Aceto-β-naphthylmethylamide, $C_{10}H_7 \cdot N(CH_3) \cdot CO \cdot CH_3$, was prepared by mixing β-naphthylmethylamine (1 mol.) and acetic

anhydride (1·5 mols.). The product when crystallised from light petroleum (b. p. 40—60°) separated in colourless, rhombic prisms melting at 50—51°:

0·1523 gave 9·6 c.c. N_2 at 16° and 751·5 mm. N = 7·28.

$C_{13}H_{13}ON$ requires N = 7·04 per cent.

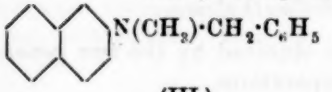
Benzo-β-naphthylmethylamide, $C_{10}H_7 \cdot N(CH_3) \cdot CO \cdot C_6H_5$, produced by the Schotten-Baumann reaction, crystallised from light petroleum in colourless needles melting at 84°:

0·2663 gave 11·3 c.c. N_2 at 20° and 762 mm. N = 4·88.

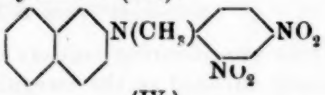
$C_{18}H_{15}ON$ requires N = 5·36 per cent.

Toluene-p-*sulphon*-β-*naphthylmethylamide*.—This compound, which has already been described as resulting from the methylation of toluene-*p*-sulphon-β-naphthylamide (Morgan and Micklethwait, T., 1912, **101**, 150), was prepared more directly by grinding together β-naphthylmethylamine, toluene-*p*-sulphonyl chloride, and fused sodium acetate in approximately molecular proportions. The crude product, after digestion with aqueous sodium carbonate, was crystallised from alcohol, and separated in colourless, arborescent needles melting at 73° (T., 1912, *ibid.*, colourless needles, m. p. 77—78°).

Benzyl-β-naphthylmethylamine (III).



(III.)



(IV.)

β-Naphthylmethylamine (1 mol.) and benzyl chloride (1·25 mols.) were mixed and heated with 10 per cent. aqueous sodium hydroxide (1·25 mols.) in a reflux apparatus for several hours until the solid product of the mixture of the two organic reagents had been decomposed. On cooling, a brown, solid mass separated consisting of crude benzyl-β-naphthylmethylamine (yield, 70 per cent.). This base was soluble in benzene, acetone, or alcohol, and crystallised in lustrous, colourless needles melting at 82—83°:

0·3358 gave 15·8 c.c. N_2 at 17° and 765 mm. N = 5·51.

$C_{18}H_{17}N$ requires N = 5·67 per cent.

Like all the other known dialkyl-β-naphthylamines, this tertiary base did not couple with diazonium salts.

2:4-*Dinitrophenyl-β-naphthylmethylamine* (IV).

Molecular proportions of β-naphthylmethylamine and 4-chloro-1:3-dinitrobenzene were dissolved in alcohol, and the solution was

heated under reflux with fused sodium acetate for two to three hours. The crystalline product separating from the cooled solution was washed successively with alcohol and water to remove 4-chloro-1:3-dinitrobenzene and sodium salts respectively. The final residue was crystallised from benzene or acetic acid, from which it separated in orange-red, elongated prisms melting at 183°:

0·1630 gave 18·2 c.c. N_2 at 18° and 756 mm. N = 12·88.
$C_{17}H_{13}O_4N_3$ requires N = 13·00 per cent.

2:4-*Dinitrophenylnitro-β-naphthylmethylamine*, $NO_2 \cdot C_{10}H_6 \cdot N(CH_3) \cdot C_6H_3(NO_2)_2$.—The preceding dinitro-compound was dissolved in the least possible amount of glacial acetic acid and treated with sufficient nitric acid (D 1·42), diluted with an equal volume of glacial acetic acid, to introduce one nitro-group. The solution was stirred thoroughly, warmed, and left overnight in the ice-chest, when a mass of yellow crystals separated. This product crystallised from alcohol in yellow flakes and melted at 156—157°:

0·1080 gave 14·7 c.c. N_2 at 22° and 761 mm. N = 15·52.
$C_{17}H_{12}O_6N_4$ requires N = 15·22 per cent.

The authors' thanks are due to the British Dyestuffs Corporation (Manchester) for the starting materials employed in this investigation.

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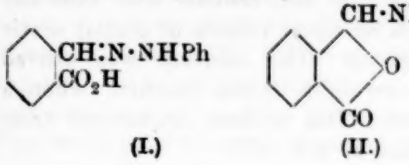
CI.—*Action of Phenylhydrazine on Phthalaldehydic and Phthalonic Acids: Phenyl-hydrazo- and Azo-Phthalide.*

By Prafulla Chandra Mitter and Jnanendra Nath Sen.

In a previous communication (T., 1917, **111**, 988) the authors have shown that by the action of phenylhydrazine on opianic and nitro-opianic acids in ethereal solution derivatives of hydrazophthalide are formed, which can be oxidised by mercuric oxide to azo-phthalides. In the case of phthalonic acid definite indications of the formation of hydrazo- and azo-phthalide derivatives were obtained, although the products could not then be isolated. It has

now been found that on adding a solution of phenylhydrazine hydrochloride to a nearly neutral solution of phthalonic acid the phenylhydrazone is obtained, which on treatment with dilute hydrochloric acid is converted into phenylphthalazonecarboxylic acid identical with the anhydrophenylhydrazine-*o*-carboxyphenylglyoxylic acid prepared by Henriques (*Ber.*, 1888, **21**, 1610).

In the case of phthalaldehydic acid, treatment with phenylhydrazine hydrochloride under similar conditions gives phenylhydrazophthalide, which can be oxidised in acetone solution by mercuric acetamide to phenylazophthalide. Treatment with acetic acid converts the hydrazophthalide into phenylphthalazone (Racine, *Annalen*, 1887, **239**, 80):



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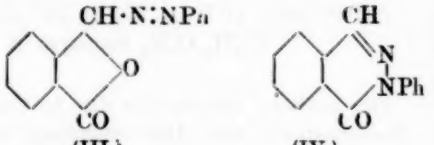

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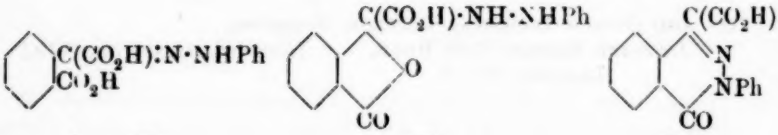

(V.) (VI.) (VII.)

Experimental.

Phenylhydrazone of Phthalaldehydic Acid (I).

On account of the great solubility of the phenylhydrazine derivative in ether, the compound was prepared by the action of phenylhydrazine hydrochloride on the sodium salt of phthalaldehydic acid.

Phthalaldehydic acid (1·5 grams: 1 mol.) was dissolved in sodium carbonate solution (0·75 mol.), and to this an aqueous solution of phenylhydrazine hydrochloride (1·45 grams: 1 mol.) was added. The phenylhydrazine derivative separated almost immediately as a canary-yellow powder in almost quantitative yield (2·7 grams). On crystallisation from slightly warm dilute alcohol it was obtained in pale yellow needles melting at 106°, which turned pink on exposure

to air. It dissolves readily in sodium hydrogen carbonate solution or ammonia. Acetic acid transforms it into the cyclic compound:

0·1065 gave 0·2741 CO_2 and 0·0476 H_2O. C = 70·19; H = 4·97.
0·1011 „ 10·3 c.c. N_2 at 24° and 760 mm. N = 11·79.
$C_{14}H_{12}O_2N_2$ requires C = 70·00; H = 5·00; N = 11·66 per cent.

The substance was dissolved in alcohol and titrated with standard alkali. It was found to be monobasic:

0·1373 required 5·65 c.c. of *N*/10-alkali, whilst this weight of a monobasic acid of the above formula requires 5·70 c.c.

Phenylazophthalide.

Phenylhydrazophthalide (II, 0·55 gram) was dissolved in about 20 c.c. of pure acetone, 2 grams of pure recrystallised mercuric acetamide were added, and the mixture was heated on the water-bath under reflux for about three hours. The colour of the solution gradually changed to deep yellow. The solution was filtered, the residue washed with acetone, and the washings added to the filtrate. The filtrate was evaporated to dryness and the residue washed with dilute sodium carbonate solution and water, and then dissolved in acetone. On adding water a small quantity of tarry matter was precipitated, which was removed by filtration. Further addition of water precipitated the azo-compound (III) in yellow plates melting at 149—150°. The substance is insoluble in sodium carbonate, and gives with concentrated sulphuric acid a purple coloration. The alcoholic solution is yellow with a green shade, and the colour changes to pink on the addition of alkali.

The compound dissolves readily in acetone or benzene:

0·1581 gave 0·4132 CO_2 and 0·0612 H_2O. C = 71·05; H = 4·30.
0·1025 „ 10·5 c.c. N_2 at 24° and 760 mm. N = 11·86.
$C_{14}H_{10}O_2N_2$ requires C = 70·49; H = 4·20; N = 11·77 per cent.

Phenylphthalazone (IV).

Phenylhydrazophthalide is warmed with a small quantity of glacial acetic acid for a few minutes and hot water is added. The phthalazone is readily obtained in fine needles with a pale pink colour melting at 105°. It is insoluble in alkali even on boiling. (Found: N = 13·11. $C_{14}H_{10}ON_2$ requires N = 12·61 per cent.)

Phthalonic Acid and Phenylhydrazine.

Phthalonic acid (1 gram: 1 mol.) was dissolved in water containing sodium carbonate (0·42 gram: 0·75 mol.), and a solution of

phenylhydrazine hydrochloride (1·5 grams: 2 mols.) in water was added. The phenylhydrazine derivative (V or VI) separated at once in crystalline flakes melting at 171—172°. It dissolves readily in acetone or alcohol, but on the addition of water the solution deposits an oil. All attempts at recrystallisation failed:

0·0938 gave 0·2167 CO_2 and 0·0360 H_2O. C = 63·06; H = 4·27.
0·1169 „ 9·6 c.c. N_2 at 23° and 760 mm. N = 9·73.
$C_{15}H_{12}O_4N_2$ requires C = 63·38; H = 4·23; N = 9·85 per cent.

The substance was dissolved in dilute alcohol and titrated with standard alkali. It was found to be dibasic:

0·1449 required 9·4 c.c. of *N*/10-alkali, whilst this weight of a dibasic acid of the above molecular formula requires 10·2 c.c.

The substance gradually turns brownish-yellow on exposure to air. Attempts at oxidation with mercuric acetamide did not yield any pure product.

Phenylphthalazonecarboxylic Acid (VII).

The mother liquor after the filtration of the hydrazo-compound deposits, on keeping, long needles with a silky lustre dissolving readily in sodium carbonate solution and melting at 210°. The same substance is also obtained by keeping the hydrazophthalidecarboxylic acid suspended in dilute hydrochloric acid. (Found, C = 67·08; H = 3·63; N = 10·10. $C_{15}H_{10}O_3N_2$ requires C = 67·67; H = 3·76; N = 10·05 per cent.

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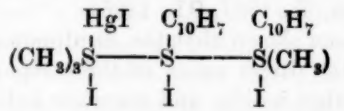
CII.—*Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part VII. Chain Compounds of Sulphur* (continued).

By SIR PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA.

IN Part IV. of this series (this vol., p. 261), among the products of the interaction of phenyl mercaptan and mercuric nitrite which were isolated, was one having the empirical formula Ph_2S_3Hg. When α-naphthyl mercaptan is treated with mercuric nitrite only one product is obtained, which is the exact analogue of the former, namely, $(C_{10}H_7)_2S_3Hg$. This, like the benzenoid derivative, is

soluble in hot benzene, and can therefore be easily obtained in a state of purity.

The action of methyl iodide on the compound Ph_2S_3Hg leads to a trisulphonium compound in which all the sulphur atoms are quadrivalent (compare Part IV.). The action of alkyl iodides on the new compound, $(C_{10}H_7)_2S_3Hg$, has proved to be of much interest. With methyl iodide, for instance, three sulphonium derivatives, tri-, di-, and mono-, are formed together. The trisulphonium compound (I) contains two sexavalent and one quadrivalent sulphur atoms. The



(I.)

monosulphonium derivative also contains a sexavalent sulphur atom, and all the monosulphonium compounds described in the present paper are of this category.

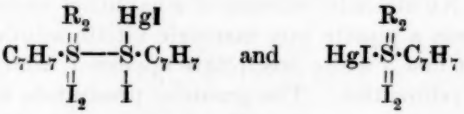
The action of *p*-tolyl mercaptan on mercuric nitrite has also been studied. The mercaptide nitrite corresponds with the formula $C_7H_7\cdot S(hg)(HgNO_2)\cdot S\cdot C_7H_7$, or preferably

$$C_7H_7\cdot S(hg){:}S(HgNO_2)\cdot C_7H_7.$$

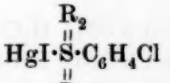
p-Chlorophenyl mercaptan also yields a compound of exactly the same type. That they are definite compounds is proved by the fact that successive crops from hot benzene solution have the same melting point and composition.

The mercaptide nitrite obtained from *p*-tolyl mercaptan reacts with methyl and ethyl iodides, yielding in each case a mono- and a di-sulphonium compound, the sulphur atoms of the latter being sexavalent (compare Part VI., this vol., p. 548):

$$C_7H_7\cdot S(hg){:}S(HgNO_2)\cdot C_7H_7 \xrightarrow{RI}$$



The mercaptide nitrite from *p*-chlorophenyl mercaptan gives with alkyl iodides only one monosulphonium compound of the type:



In Part VI. of this series one of us has described disulphonium compounds containing one or both of the atoms of sulphur in the

sexavalent condition. The present work not only corroborates the existence of this class of compounds, but goes a step further in that a trisulphonium compound is described containing two sexavalent and one quadrivalent sulphur atoms.

In addition to the monosulphonium compounds described in the present paper, another series has been prepared, namely, that obtained by the reaction of ethyl sulphide and mercuric iodide with the higher and lower homologues of ethyl iodide, and in each case a compound of the type Et_2S,RI,HgI_2 has been obtained (compare Smiles and Hilditch, T., 1907, **91**, 1396).

It has already been shown that the disulphonium compounds can be synthesised by the direct union of the components, for example, ethyl disulphide, ethyl iodide, and mercuric iodide (T., 1916, **109**, 611). By substituting, however, the other alkyl iodides the corresponding members of the series have been obtained, with this difference, that an interchange of radicles invariably takes place. Thus, when a mixture of ethyl disulphide and mercuric iodide is treated with an alkyl iodide, RI, compounds of the type $EtRS_2,HgI_2,RI$ are formed. Again, when a mercaptide nitrite like the compound $EtS{\cdot}HgNO_2$ is treated with an alkyl iodide, RI, by an interchange of radicles, the compound $EtRS_2,HgI_2,RI$ is obtained (*loc. cit.*). It is thus seen that either mode of formation yields the same compound, the interchange of radicles being thus the most prominent feature. There is, however, this marked difference that in the monosulphonium series no such interchange of radicles has been found to take place.

Experimental.

Interaction of α-Naphthyl Mercaptan and Mercuric Nitrite: Formation of the Compound $(C_{10}H_7)_2S_3Hg$.

An alcoholic solution of α-naphthyl mercaptan was slowly dropped from a pipette into mercuric nitrite solution with constant shaking. At first a white precipitate appeared, which, however, soon acquired a yellow tint. The granular precipitate was collected, washed, and dried in a vacuum. For further purification it was crystallised from boiling benzene, in which it was fairly readily soluble, and then melted at 198°:

0·1118 gave 0·1827 CO_2 and 0·0344 H_2O. C = 44·57; H = 3·43.
0·1200 ,, 0·0459 Hg and 0·1354 $BaSO_4$. Hg = 37·93; S = 15·38.
$C_{20}H_{14}S_3Hg$ requires C = 43·63; H = 2·54; Hg = 36·36; S = 17·45 per cent.

Interaction of the Compound $(C_{10}H_7)_2S_3Hg$ *and Methyl Iodide: Formation of the Trisulphonium Compound* (I).

The method of procedure is exactly the same as in the interaction of simple mercaptide nitrites and alkyl iodides. After heating with methyl iodide under reflux, the mixture was allowed to cool. Within half an hour, the heavy, oily liquid at the bottom began to solidify to well-defined crystals, which were collected. The substance was insoluble in acetone, and was therefore washed several times with this solvent. Finally, it was recrystallised from hot methyl alcohol, when dull yellow crystals melting at 113° were obtained. Both the soluble and insoluble varieties of this series of sulphonium compounds dissolve readily in boiling methyl alcohol, and thus all of them have been obtained in a pure condition:

0·2196 gave 0·2219 CO_2 and 0·0574 H_2O. C=27·56; H=2·90.
0·3016 ,, 0·0540 Hg ,, 0·2484 AgI. Hg=17·91; I=44·15.
0·3729 ,, 0·2223 $BaSO_4$. S=8·19.

$C_{26}H_{32}I_4S_3Hg$ requires C=27·18; H=2·79; Hg=17·42; I=44·26; S=8·36 per cent.

The filtrate, after the separation of the above insoluble compound, was freed from excess of methyl iodide by evaporation. The oily residue was dissolved in acetone, the solution filtered, concentrated to a small bulk, and excess of ether added, when a yellow oil was again precipitated. The oil was dissolved in boiling methyl alcohol, and on slowly cooling, yellow needles with a faint green tint separated. From the methyl alcoholic solution five successive crops were obtained by fractional crystallisation. Of these, the first two crops melted at 102°; they were therefore mixed and again crystallised from the above solvent, when the product melted at the same temperature. This was the sexavalent monosulphonium compound and gave the following results on analysis:

0·1496 gave 0·1058 CO_2 and 0·0284 H_2O. C=19·29; H=2·11.
0·3927 ,, 0·1023 Hg ,, 0·3524 AgI. Hg=26·05; I=48·48.
0·2650 ,, 0·0693 Hg. Hg=26·12.

$C_{12}H_{13}I_3SHg$ requires C=18·7; H=1·82; Hg=25·97; I=49·5 per cent.

The mother liquor from which the above five fractions were obtained began to deposit oily globules which were dissolved in acetone. On the addition of ether an oil was obtained which was kept in a vacuum over sulphuric acid for several days, but did not solidify. On stirring, however, with a little ether, crystallisation at once occurred. The compound was now purified by repeated crystal-

lisation from methyl alcohol, and when pure it melted sharply at 93°. It consisted of the disulphonium compound,

$C_{10}H_7 \cdot CH_3S_2,HgI_2,CH_3I$:

0·2020 gave 0·1418 CO_2 and 0·0332 H_2O. C = 19·14; H = 1·82.
0·2055 „ 0·0507 Hg „ 0·1750 AgI. Hg = 24·67; I = 46·02.
$C_{12}H_{13}I_3S_2Hg$ requires C = 17·95; H = 1·52; Hg = 24·93; I = 47·51 per cent.

As was to be expected, an interchange of radicle takes place in this case.

Interaction of the Compound $(C_{10}H_7)_2S_3Hg$ *and Propyl Iodide: Formation of the Monosulphonium Compound,* $C_{10}H_7 \cdot SI_2(C_3H_7)_2 \cdot HgI$.

From methyl-alcoholic solution the compound was deposited as an oil which, when kept in a vacuum for a week, solidified. It was then further purified by recrystallisation from methyl alcohol, when it melted at 106°:

0·1345 gave 0·1173 CO_2 and 0·0334 H_2O. C = 23·82; H = 2·76.
0·3701 „ 0·0900 Hg „ 0·3101 HgI. Hg = 24·32; I = 45·28.
$C_{16}H_{21}I_3SHg$ requires C = 23·25; H = 2·54; Hg = 24·21; I = 46·13 per cent.

Mercuric Nitrite and p-*Tolyl Mercaptan: Formation of the Compound* $C_7H_7 \cdot S(hg) \cdot S(HgNO_2) \cdot C_7H_7$.

On adding an alcoholic solution of the mercaptan to the mercuric nitrite solution a product is obtained which on allowing to remain and occasionally stirring forms a dull yellow, granular mass. This is purified by crystallisation from hot benzene. Three successive crops melted at 127°. The purity of the compound is thus unquestionable. It evolves nitrous fumes when treated with hydrochloric acid:

0·0937 gave 0·0982 CO_2 and 0·0234 H_2O. C = 28·58; H = 2·77.
0·1419 „ 3·2 c.c. N_2 at 25° and 760 mm. N = 2·43.
0·1316 „ 0·0737 HgS. Hg = 48·27.
$C_{28}H_{28}O_4N_2S_4Hg_3$ requires C = 28·38; H = 2·36; N = 2·36; Hg = 50·68 per cent.

Interaction of the Mercaptide Nitrite of p-*Tolyl Mercaptan and Methyl Iodide: Formation of the Compounds* $C_7H_7 \cdot SMe_2I_2 \cdot SI(C_7H_7) \cdot HgI$ *and* $C_7H_7 \cdot SMe_2I_2 \cdot HgI$.

A clear solution was obtained in this case on digesting the mercaptide nitrite with methyl iodide for three or four minutes. After

evaporating the excess of methyl iodide the oily residue was dissolved in acetone and the solution filtered. On concentrating and cooling, a small quantity of yellowish-white, scaly crystals began to be deposited. The compound was collected and washed with a small quantity of cold acetone. On recrystallising from hot methyl alcohol it melted sharply at 109°. The filtrate on evaporation of the acetone, left an oily residue, which was dissolved in methyl alcohol. On slow evaporation of the solvent, needle-shaped, yellow crystals melting at 121° were obtained.

The *disulphonium* compound melting at 109° gave the following results on analysis:

0·1656 gave 0·1215 CO_2 and 0·0428 H_2O. C = 20·08; H = 2·87.
0·3418 „ 0·0735 Hg „ 0·2950 AgI. Hg = 21·50; I = 46·63.
$C_{16}H_{20}I_4S_2Hg$ requires C = 19·51; H = 2·03; Hg = 20·32; I = 51·63 per cent.

The *monosulphonium* compound melting at 121° gave the following results:

0·2718 gave 0·1440 CO_2 and 0·0686 H_2O. C = 14·45; H = 2·80.
0·4152 „ 0·1132 Hg „ 0·3912 AgI. Hg = 27·27; I = 50·91.
$C_9H_{13}I_3SHg$ requires C = 14·51; H = 1·75; Hg = 27·25; I = 51·90 per cent.

Interaction of the Mercaptide Nitrite of p-*Tolyl Mercaptan and Ethyl Iodide: Formation of the Compounds* $C_7H_7{\cdot}SEt_2I_2{\cdot}SI(C_7H_7){\cdot}HgI$ *and* $C_2H_5{\cdot}C_6H_4{\cdot}SEt_2I_2{\cdot}HgI$.

The method of procedure was exactly the same as described above. The *disulphonium* compound melts at 120°:

0·1235 gave 0·0240 Hg and 0·1111 AgI. Hg = 19·43; I = 48·63.
$C_{18}H_{24}I_4S_2Hg$ requires Hg = 19·76; I = 50·20 per cent.

The *monosulphonium* compound melts at 70°:

0·1387 gave 0·0946 CO_2 and 0·0320 H_2O. C = 18·60; H = 2·54.
0·2943 „ 0·0746 Hg „ 0·2641 AgI. Hg = 25·70; I = 48·50.
$C_{12}H_{16}I_3SHg$ requires C = 18·50; H = 2·44; Hg = 25·77; I = 49·09 per cent.

Interaction of the Mercaptide Nitrite of p-*Tolyl Mercaptan and Propyl Iodide: Formation of the Monosulphonium Compound,* $C_7H_7{\cdot}SI_2(C_3H_7)_2{\cdot}HgI$.

In this case also (compare p. 1151) the compound could not be brought into the solid condition until it had been kept in a vacuum

desiccator for some days. Finally, it was crystallised from methyl alcohol, when it melted at 71°:

0·1670 gave 0·1193 CO_2 and 0·0425 H_2O. C = 19·48; H = 2·83.
0·3006 ,, 0·0764 Hg and 0·2520 AgI. Hg = 25·42; I = 45·30.
$C_{13}H_{21}I_3SHg$ requires C = 19·75; H = 2·66; Hg = 25·32; I = 48·23 per cent.

Interaction of p*-Chlorophenyl Mercaptan and Mercuric Nitrite: Formation of the Compound* $C_6H_4Cl\cdot S(hg):S(HgNO_2)\cdot C_6H_4Cl$.

This compound was crystallised from boiling benzene solution:

0·3576 gave 0·1662 Hg and 0·1600 AgCl. Hg = 46·47; Cl = 11·07.
$C_{24}H_{16}O_4N_2Cl_4Hg_3$ requires Hg = 47·39; Cl = 11·22 per cent.

Interaction of the Mercaptide Nitrite of p*-Chlorophenyl Mercaptan and Methyl Iodide: Formation of the Compound* $C_6H_4Cl\cdot SMe_2I_2\cdot HgI$.

This crystallised from hot methyl alcohol in yellow needles melting at 129°:

0·2647 gave 0·1202 CO_2 and 0·0400 H_2O. C = 12·38; H = 1·68.
0·3591 ,, 0·0945 Hg, 0·4118 AgI + AgCl, and 0·2863 AgCl by chlorination. Hg = 26·32; I = 48·47; Cl = 6·19.
$C_8H_{10}ClI_3SHg$ requires C = 12·73; H = 1·33; Hg = 26·51; I = 50·49; Cl = 4·70 per cent.

The corresponding *ethyl* compound was at first deposited as an oil, but, when purified by repeated crystallisation, formed a yellow powder melting at 64°:

0·2796 gave 0·1446 CO_2 and 0·0495 H_2O. C = 14·11; H = 1·77.
0·4310 ,, 0·1100 Hg, 0·4506 AgI + AgCl, and 0·3051 AgCl by chlorination. Hg = 25·52; I = 46·83; Cl = 4·42.
$C_{10}H_{14}ClI_3SHg$ requires C = 15·34; H = 1·79; Hg = 25·57; I = 48·71; Cl = 4·54 per cent.

Reaction of Ethyl Sulphide and Mercuric Iodide with Alkyl Iodides.

A mixture of ethyl sulphide and ethyl iodide was heated under reflux with an excess of mercuric iodide, when a golden-yellow liquid was obtained. It was dissolved in a minimum quantity of acetone and precipitated by ether and the process repeated. A yellow, crystalline powder was obtained, which melted at 110°. A small quantity remained insoluble in acetone and melted at 146—147° (com-

pare Part VI). The compound melting at 110° gave the following results:

0·1984 gave 0·0757 CO_2 and 0·0427 H_2O. C=10·41; H=2·39.
0·2775 „ 0·0764 Hg „ 0·2708 AgI. Hg=27·53; I=52·74.
$C_6H_{15}I_3SHg$ requires C=10·29; H=2·14; Hg=28·57; I=54·43 per cent.

A mixture of ethyl sulphide and methyl iodide was treated with excess of mercuric iodide as above. The yellow, crystalline product melted at 65—67°:

0·2652 gave 0·0862 CO_2 and 0·052 H_2O. C=8·86; H=2·180.
0·5518 „ 0·1595 Hg „ 0·5347 AgI and 0·1480 $BaSO_4$. Hg=28·91; I=52·36; S=3·68.
$C_5H_{13}I_3SHg$ requires C=8·75; H=1·90; Hg=29·15; I=55·53; S=4·67 per cent.

The corresponding yellow, crystalline *propyl* derivative melted at 88—89°:

0·1904 gave 0·0861 CO_2 and 0·0480 H_2O. C=12·33; H=2·81.
0·3796 „ 0·1038 Hg „ 0·3569 AgI. Hg=27·35; I=50·83.
$C_7H_{17}I_3SHg$ requires C=11·77; H=2·38; Hg=28·00; I=53·36 per cent.

The corresponding yellow, crystalline *butyl* derivative melted at 72—73°:

0·3829 gave 0·1874 CO_2 and 0·0673 H_2O. C=13·35; H=1·95.
0·5745 „ 0·1565 Hg. Hg=27·24.
$C_8H_{19}I_3SHg$ requires C=13·19; H=2·61; Hg=27·47 per cent.

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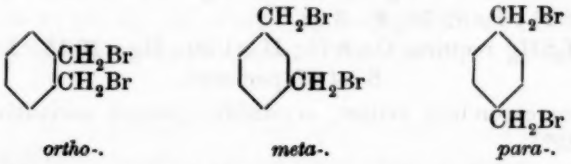
CIII.—*Asymmetric Replacement in the* meta-*Series. Part I.*

By WILLIAM HENRY GOUGH and JOCELYN FIELD THORPE.

THE interaction of organic halogen derivatives containing two atoms of the halogen and substances of the type of potassium cyanide usually leads to the replacement of both halogen atoms and the consequent production of the corresponding dinitriles. If an insufficient quantity of potassium cyanide is present completely to effect this change, it generally happens that the whole of the cyanide is utilised in forming the dinitriles and the rest of the

dihalogen derivatives remains unaltered. This is, at any rate, the usual course of the reaction when the halogen atoms are symmetrically placed in the organic molecule, although it is obvious that asymmetric substitution, that is, the successive replacement of the halogen atoms, with the intermediate formation of the compound in which only one halogen atom is substituted, can and does take place when the halogen atoms are in positions in the organic molecule which cause them to possess different degrees of reactivity, and therefore render one of them more open to attack than the other.

There is thus no reason to suppose that the three $\omega\omega'$-dibromoxylenes (xylylene dibromides), in each of which the bromine atoms



ortho-. *meta-*. *para-*.

are symmetrically placed to each other, would exhibit any fundamental differences in their behaviour towards alcoholic potassium cyanide under the same experimental conditions, and yet the evidence brought forward in this communication shows clearly that whereas the *o*- and *p*-compounds are converted directly into the dinitriles without any intermediate formation of the bromonitriles, $C_6H_4(CH_2Br)\cdot CH_2\cdot CN$—even though an insufficient quantity of potassium cyanide to form the dinitrile is present—the bromine atoms in the meta-compound can be easily replaced successively, and that it is a simple matter to prepare the *m*-bromo-nitrile, of the above formula, in considerable quantities. In other words, the reaction between $\omega\omega'$-dibromo-*o*-(or *p*-)xylene and alcoholic potassium cyanide (equal molecules) is represented by equation (1), whereas equation (2) represents the reaction in the case of the meta-compound:

(1) $2C_6H_4(CH_2Br)_2 + 2KCN = C_6H_4(CH_2\cdot CN)_2 + C_6H_4(CH_2Br)_2 + 2KBr.$

(2) $C_6H_4(CH_2Br)_2 + KCN = C_6H_4(CH_2Br)\cdot CH_2\cdot CN + KBr.$

It is certainly remarkable that this property of the meta-compound should have been hitherto unrecognised, because the conversion of all three $\omega\omega'$-dibromoxylenes into the nitriles has been carried out by several investigators. Indeed, it was while we were attempting to prepare the *m*-dinitrile by what we understood to be Kipping's method that the isolation of this intermediate product occurred. It happens that the reference to Kipping's paper is quoted wrongly in "Beilstein," and the details of the preparation given there, which are evidently taken from the paper by Oddo

(*Gazzetta*, 1893, **23**, ii, 338), state that twenty hours on the water-bath are sufficient to convert 13·4 grams of $\omega\omega'$-dibromo-*m*-xylene, 9 grams of potassium cyanide, and 500 c.c. of alcohol completely into the dinitrile and potassium bromide. As a matter of fact, in our hands these conditions led to a 90 per cent. yield of the pure *m*-bromo-nitrile, and we were unable to isolate any trace of the dinitrile. A subsequent reference to Kipping's paper (T., 1888, **53**, 41) showed that he had heated his reaction mixture on the water-bath for a "considerable time." It is certain, moreover, that Kipping's product could not have contained any appreciable quantity of the bromo-nitrile, because he found that the crude oil formed in his reaction gave an almost theoretical yield of *m*-phenylenediacetic acid when it was hydrolysed by alcoholic potassium hydroxide (*ibid.*, p. 43).

It seemed therefore desirable to carry out a series of comparative experiments on the behaviour of the three $\omega\omega'$-dibromoxylenes towards potassium cyanide under different conditions in order to ascertain whether this property of asymmetric replacement was characteristic of the meta-series, and whether, in fact, we had to hand another example of abnormal behaviour in these derivatives.

$\omega\omega'$-Dibromo-*o*-xylene has been converted into the dinitrile by Baeyer and Pape (*Ber.*, 1884, **17**, 447); similar conditions were subsequently employed by Moore and Thorpe (T., 1908, **93**, 175) for the preparation of large quantities of the compound. When 10 per cent. more than the amount of potassium cyanide, representing two molecular proportions, is used and the quantity of the solvent is reduced to a minimum, the reaction proceeds smoothly and is finished at the end of an hour, the heat generated being sufficient to carry the change to completion.

The yield is good, and the only by-product accompanying the dinitrile is a small quantity of oily impurity of indefinite character; no trace of the bromo-nitrile can be detected.

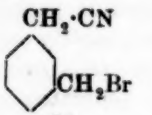
The interaction of one molecular proportion of $\omega\omega'$-dibromo-*o*-xylene and one of potassium cyanide was investigated by Moore and Thorpe during the earlier experiments (*loc. cit.*), but the details were not then published, because the preparation of the intermediate bromo-nitrile, which was the object in view, was not achieved. A description of this work is now included in the experimental portion of this paper; it shows clearly that the reaction proceeds in accordance with equation (1) above.

p-Phenylenediacetonitrile has been prepared by Klippert (*Ber.*, 1876, **9**, 1766) from $\omega\omega'$-dichloro-*p*-xylene, and by Kipping (T., 1888, **53**, 44) from the corresponding dibromo-derivative. Kipping found that the yield of the dinitrile was only approximately 50 per

cent. of the theoretical, the remainder of the product being an amorphous substance of resinous character; we agree with him that it does not appear possible to avoid the formation of this resin or to increase the yield of the dinitrile by varying the conditions. The reaction under his conditions proceeds smoothly, but requires a longer time than is the case with the ortho-derivative; no trace of the bromo-nitrile is formed.

When one molecular proportion of $\omega\omega'$-dibromo-*p*-xylene and one of potassium cyanide are employed, the reaction proceeds in accordance with equation (1), approximately 50 per cent. of the dibromo-compound being recovered unchanged and the remainder being converted into the dinitrile.

The references in connexion with the preparation of *m*-phenylene-diacetonitrile have already been given, and we have stated that, in our hands, the published experimental conditions led to the formation of the *m*-bromo-nitrile (I) as sole product. The constitution of this substance has been placed beyond question by its conversion into the already known $\omega\omega'$-dihydroxy-*m*-xylene (II) (Colson, *Ann. Chim. Phys.*, 1885, [vi], **6**, 112) by the action of freshly precipitated silver hydroxide. We have also further characterised it by the formation of the hydroxy-nitrile (III), the hydroxy-acid (IV), the ethoxy-derivative (V), and the acid (VI) which is formed by condensing it with the sodium compound of ethyl malonate and hydrolysing the product. Experiments were also carried out in order



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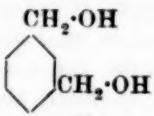

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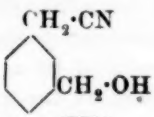

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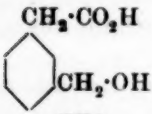

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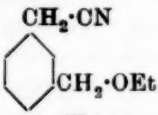

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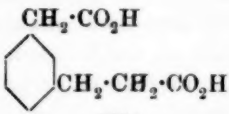

(VI.)

to ascertain whether the state of dilution of the potassium cyanide had any influence on the course of the reaction in the three series, but this was found not to be the case, and it is evident, therefore, that the property of asymmetric replacement in a compound possessing apparent symmetry is characteristic of the meta-series.

Experimental.

The Interaction of Alcoholic Potassium Cyanide (1 *mol.*) *and* ωω′-*Dibromo*-o-(*and* p-)*xylene* (1 *mol.*).

ωω′-*Dibromo*-o-*xylene*.—This operation was carried out in a manner similar to that described in the earlier paper (Moore and Thorpe, T., 1908, **93**, 175), but care was taken to keep, as far as possible, to the theoretical amounts required by equation (1) (p. 1156).

Fifty-three grams of pure ωω′-dibromo-*o*-xylene melting at 95°, and in a finely ground condition, were added gradually to a boiling solution containing 13 grams of Kahlbaum's purest potassium cyanide, which had been prepared by dissolving the cyanide in the smallest possible amount of cold water and adding three times the volume of absolute alcohol. When all the dibromide had been added, the mixture was allowed to remain for half an hour, when it was diluted with water, and the oil, which was then precipitated, extracted with ether. The dried ethereal solution was freed from the solvent, and the oily residue submitted to careful fractionation under diminished pressure (20 mm.). The fraction boiling below 160° was then redistilled, and the portion boiling between 135° and 140° collected. The distillate solidified, and was found to melt, without further purification, at 94—95°. An analysis (Found: Br = 60·71. $C_8H_8Br_2$ requires Br = 60·6 per cent.) proved it to be pure ωω′-dibromo-*o*-xylene. The amount recovered weighed 24·7 grams, or, in other words, it represented approximately 50 per cent. of the dibromo-compound originally used.

ωω′-*Dibromo*-p-*xylene*.—In this case, the same conditions and quantities as those given above were used, excepting that, after all the dibromide had been added, the mixture was heated on the water-bath for four hours. Fractionation of the oily product gave a quantity of distillate boiling below 160°/20 mm., and this on redistillation gave 25 grams of liquid boiling at 145°/21 mm., which rapidly solidified in the receiver. The solid melted, without further purification, at 143°, and an analysis (Found: Br = 60·56. $C_8H_8Br_2$ requires Br = 60·6 per cent.) proved it to be pure ωω′-dibromo-*p*-xylene. In this case also it is evident that the reaction had proceeded in accordance with equation (1) (p. 1156), and that approximately 50 per cent. of the dibromo-compound had been recovered unchanged.

The residue left in the flask after the ωω′-dibromo-*o*-xylene had been distilled off, together with a small quantity obtained on subsequently refractionating the distillate, solidified on cooling, and

when recrystallised from alcohol yielded 14·5 grams of pure *o*-phenylenediacetonitrile melting at 60°. On the other hand, the residues from the ωω′-dibromo-*p*-xylene experiment, which also solidified on cooling, gave only 8 grams of the dinitrile melting at 98° when recrystallised.

*The Interaction of ωω′-Dibromo-*m*-xylene and Alcoholic Potassium Cyanide under Different Conditions.*

(1) *Experiments involving the Use of ωω′-Dibromo-*m*-xylene* (1 mol.) and Potassium Cyanide (2 mols.).* (a) *Oddo's Method (loc. cit.).*

ωω′-Dibromo-*m*-xylene (13·4 grams) and 9 grams of potassium cyanide (pure and finely ground) were mixed with 500 c.c. of alcohol and heated in a flask fitted with a reflux condenser for twenty hours on the water-bath. The alcohol was then distilled off and water added, the precipitated oil and aqueous liquid being extracted by ether. The washed and dried ethereal solution yielded an oil on evaporating the solvent, which, when distilled under 18 mm. pressure, gave 9·5 grams of a colourless oil boiling at 140—141°. This oil appeared to be the sole product of the reaction.

(*b*) The quantities and conditions employed in this case were based on those used by Atkinson and Thorpe (T., 1907, **91**, 1699) for the production of the three tolylacetonitriles. Sixty grams of pure, finely ground potassium cyanide were dissolved in the smallest possible quantity of water, and then diluted to 500 c.c. with alcohol. To this solution were added 50 grams of recrystallised ωω′-dibromo-*m*-xylene dissolved in 200 c.c. of alcohol. The whole was then heated on the water-bath under a reflux condenser for twenty-four hours, when it was noticed that, after the reaction had been in progress for two hours, an orange-coloured precipitate formed, the amount of which continued to increase for some time. At the end of the time specified, the alcohol was removed by distillation, water added in sufficient quantity to dissolve the potassium salts, and the mixture, after being cooled to 0°, filtered. The precipitate was then washed with hot alcohol, in which the nitrile is readily soluble, and the oil recovered from the alcohol in the usual way. It boiled at 140—141°/18 mm., and weighed 36 grams; there was no fraction of higher boiling point. The orange-coloured precipitate was purified by repeated extraction with hot alcohol and then with boiling water. It was an amorphous substance evidently of high molecular weight, since it did not melt and was insoluble in all the

* In all the experiments described in this section pure ωω′-dibromo-*m*-xylene melting at 76—77° was used.

usual organic solvents. An analysis showed it to contain N = 10·4 per cent., but we have not as yet been able to assign any constitution to it. Its formation was evidently due to the large excess of potassium cyanide used in the reaction.

(*c*) Finally, an experiment was carried out in order to see whether the dilution of the potassium cyanide had any important influence on the nature of the product, the proportions used being the same as those given by Oddo. Thus, 53·6 grams of the dibromo-compound and 36 grams of potassium cyanide were taken, together with 500 c.c. of alcohol, that is, about one-fourth the quantity used by Oddo, the reaction being carried out in precisely the same way as described in experiment (*a*). Here again the sole product was a colourless oil boiling at 140—141°/18 mm., the weight obtained being 38 grams.

(2) *Experiment involving the Use of ωω′-Dibromo-*m*-xylene* (1 *mol.*) *and Potassium Cyanide* (1 *mol.*).—The conditions used in this experiment were the same as those given in the case of ωω′-dibromo-*o*-(and *p*-)xylene on p. 1159, the mixture being, however, heated for ten hours on the water-bath before being worked up. In this case, the whole of the liquid product boiled at 140—141°/18 mm., that is, at practically the same temperature as the dibromo-compound used. An analysis showed, however, that it was the pure bromo-nitrile (Found: Br = 38·12. $C_8H_8Br_2$ requires Br = 60·6; C_9H_8NBr requires Br = 38·1 per cent.). The yield was almost theoretical.

*ω-Bromo-*m*-tolylacetonitrile* (I, p. 1158).

This substance, prepared by any of the methods described above, is a colourless, mobile liquid which, as already stated, boils at 140—141°/18 mm., or, with slight decomposition, at 220—221°/756 mm. The yield is approximately 90 per cent. of that theoretically possible:

0·0863 gave 0·1625 CO_2 and 0·0313 H_2O. C = 51·45; H = 4·05.

0·2099 (by Carius' method) gave 0·1879 AgBr. Br = 38·10.

0·4865 (by alcoholic $AgNO_3$) required 0·3698 $AgNO_3$. Br = 37·99.

C_9H_8NBr requires C = 51·4; H = 3·8; Br = 38·1 per cent.

An attempt to determine the nitrogen content failed, owing to the fact that the substance reacted with copper oxide at the ordinary temperature, and the combustion was therefore practically complete before the air had been swept from the tube. An estimation was carried out by Kjeldahl's method, but here again no accurate result was obtained, due doubtless to the destruction of part of the ammonia by the bromine liberated. The bromo-nitrile is in many

ways a curious compound, and is very inert towards most of the usual reagents. For example, it is not acted on by concentrated hydrochloric acid even after prolonged boiling, and is unaffected by 64 per cent. aqueous potassium hydroxide or by mild reducing agents. On the other hand, it gives a characteristic reaction with concentrated sulphuric acid, forming, even when only very small quantities are used, a deep reddish-brown solution which rapidly sets to a jelly. The action of water precipitates a yellow powder which, as the following analysis shows, possesses the same empirical formula as the original bromo-nitrile:

0·1563 gave 0·2940 CO_2 and 0·0549 H_2O. C = 51·3; H = 3·9.
0·2542 „ 0·2270 AgBr. Br = 38·0.
0·2136 „ 12 c.c. N_2 at 15° and 765·8 mm. N = 6·65.
C_9H_8NBr requires C = 51·4; H = 3·8; N = 6·7; Br = 38·1 per cent.

The structure of this substance is under investigation.

ωω'-Dihydroxy-m-*xylene* (II, p. 1158) *and ω-Hydroxy*-m-*tolylacetonitrile* (III, p. 1158).

The bromo-nitrile is readily converted into a mixture of these two substances when it is treated for half an hour with an excess of freshly precipitated silver hydroxide. The oil, which can be extracted from the product, after filtration, by ether, can be readily separated into two fractions, one boiling at 154—159°/13 mm., and another boiling at 145° under the same pressure. The former solidifies on keeping and melts at 47° (Found: C = 69·6; H = 7·2. $C_8H_{10}O_2$ requires C = 69·5; H = 7·2 per cent.). Since it readily gives *iso*phthalic acid on oxidation, it is evidently ωω'-dihydroxy-m-xylene, originally prepared by Colson (*loc. cit.*). The fraction of lower boiling point (145°/13 mm.) was analysed:

0·1403 gave 0·3770 CO_2 and 0·0770 H_2O. C = 73·3; H = 6·1.
0·1346 „ 10·95 c.c. N_2 at 16° and 762·3 mm. N = 9·54.
C_9H_9ON requires C = 73·5; H = 6·1; N = 9·5 per cent.

It is evidently *ω-hydroxy*-m-*tolylacetonitrile*, since it yields ω-hydroxy-*m*-tolylacetic acid (see below) on treatment with hydrochloric acid. The hydroxy-nitrile is a colourless, pleasant-smelling oil which decomposes when distilled under the ordinary pressure. Although their boiling points lie so close together, the separation of these two compounds by fractional distillation is complete.

ω-Hydroxy-m-*tolylacetic Acid* (IV, p. 1158).

This acid can be prepared from the above hydroxy-nitrile by boiling it with concentrated hydrochloric acid, and from the bromo-

nitrile by treatment with aqueous sulphuric acid (1:1) in a sealed tube for six hours at 150°. The acid is extracted by ether, and it is advisable to neutralise the residue, left after evaporating the ether, with dilute ammonia, and again to extract with ether, in order to remove non-acidic impurities, before finally precipitating the acid by means of hydrochloric acid. It crystallises from dilute hydrochloric acid in white, glistening plates melting at 128°:

0·1532 gave 0·3656 CO_2 and 0·0835 H_2O. C = 65·0; H = 6·05.

$C_9H_{10}O_3$ requires C = 65·1; H = 6·0 per cent.

The acid is freely soluble in alcohol, ether, or hot water.

ω-Ethoxy-m-*tolylacetonitrile* (V, p. 1158).

The bromo-nitrile (10·5 grams) is converted into this ethoxy-derivative when it is treated with an alcoholic solution of sodium ethoxide—prepared by dissolving 1·2 grams of sodium in 30 c.c. of alcohol—in the first instance at the ordinary temperature for eight hours, and finally on the water-bath for one hour. Water is then added and the oil extracted by ether, the dried ethereal solution leaving a residue on evaporation which, on distillation, yields the ethoxy-derivative as a colourless, mobile oil boiling at 161—162°/13 mm.:

0·1020 gave 0·2790 CO_2 and 0·0712 H_2O. C = 74·59; H = 7·6.

0·1285 „ 8·60 c.c. N_2 at 14° and 768·1 mm. N = 7·99.

$C_{11}H_{13}ON$ requires C = 75·4; H = 7·4; N = 8·0 per cent.

It is a remarkable fact that although the above Dumas estimation gave results in accordance with theory, and that the odour of ammonia could be detected when the compound was hydrolysed by alkali, several very careful tests by the metallic sodium method failed to reveal a trace of nitrogen.

The Condensation of Ethyl Sodiomalonate with ω-Bromo-m-*tolylacetonitrile.*

Ethyl ω-Cyano-m-*methylbenzylmalonate,*

$C_6H_4(CH_2{\cdot}CN){\cdot}CH_2{\cdot}CH(CO_2Et)_2$.

—This substance is formed by allowing a solution containing 16 grams of ethyl malonate, which has been converted into its sodium derivative by means of 1·2 grams of sodium dissolved in 30 grams of alcohol, to react with 10·5 grams of the bromo-nitrile at the temperature of the water-bath for four to five hours. It is precipitated as an oil on the addition of water, and can be extracted with ether and isolated in the usual way. The ester boils at 201—203°/18 mm.:

0·1266 gave 0·3082 CO_2 and 0·0754 H_2O. C = 66·39; H = 6·62.
0·3012 „ 12·9 c.c. N_2 at 17° and 764·4 mm. N = 4·9.
$C_{16}H_{19}O_4N$ requires C = 66·4; H = 6·6; N = 4·8 per cent.

The ester is quickly hydrolysed, by a solution containing rather more than the calculated quantity of sodium hydroxide, at a gentle heat, and the acid, $C_6H_4(CH_2{\cdot}CN){\cdot}CH_2{\cdot}CH(CO_2H)_2$, is formed as a crystalline precipitate when the solution is acidified. It was not found possible, however, to recrystallise this acid, because when its solutions in solvents are heated, carbon dioxide is quickly eliminated. If, for example, its aqueous solution is boiled, *β-ω-cyano*-m-*tolylpropionic acid*, $C_6H_4(CH_2{\cdot}CN){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, separates on cooling. This acid crystallises from water, containing a little hydrochloric acid, in white, glistening plates melting at 148°, and closely resembling anthracene in appearance:

0·1124 gave 0·2878 CO_2 and 0·0590 H_2O. C = 69·79; H = 5·90.
0·1758 „ 11·5 c.c. N_2 at 20° and 757·9 mm. N = 7·41.
$C_{11}H_{11}O_2N$ requires C = 69·8; H = 5·8, N = 7·4 per cent.

β-ω-Carboxy-m-*tolylpropionic Acid* (VI, p. 1158).

This acid is best prepared from the cyano-acid described above by dissolving it in three times its weight of concentrated sulphuric acid, allowing the solution to remain for two hours, and then, after diluting it with three times its volume of water, boiling for three hours. The acid is then collected and washed with ether, being finally recrystallised from dilute alcohol, when it is obtained in fine needles which melt at 132°:

0·1045 gave 0·2431 CO_2 and 0·0543 H_2O. C = 63·40; H = 5·82.
$C_{11}H_{12}O_4$ requires C = 63·5; H = 5·8 per cent.

The acid is sparingly soluble in hot water or ether, but readily so in alcohol. The *calcium* salt is insoluble in hot water, and the *potassium* salt crystallises from water in plates.

This work was carried out during the tenure by one of us (W.H.G.) of a fellowship granted by the Salters' Company.

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CIV.—*Molecular-weight Determination by Direct Measurement of the Lowering of the Vapour Pressure of Solutions.*

By Robert Wright.

The direct measurement of the vapour pressure of solutions has never been very extensively used as a means of determining molecular weights. The barometric method as originally employed by Raoult is too cumbersome for general use, and at the ordinary temperature the lowerings of the vapour pressure obtained with most solvents are too small to admit of accurate measurement by this means. A simple method for use with a volatile liquid, such as ether, was described in a former paper (P., 1912, **28**, 96), but it is quite unsuitable in the case of the more common solvents.

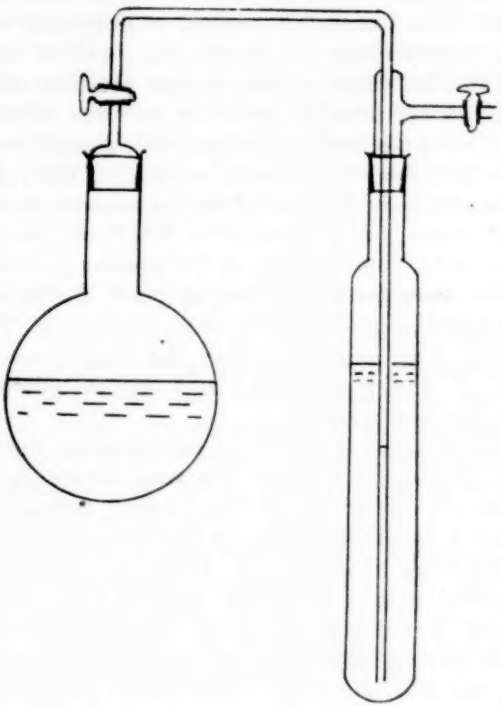
Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 1615) has described an apparatus in which the lowering of the vapour pressure produced by a solute is measured at the boiling point of the solution, the manometric liquid used being the solution itself; so that, both on account of the high temperature of the determination and the sensitiveness of the manometer, very dilute solutions can be employed in the measurements.

The apparatus about to be described resembles that of Menzies in that the solution is used as the manometric liquid, but all measurements are carried out at the ordinary temperature, and as the apparatus is of simple design, it can readily be constructed of ordinary laboratory material. A flask, or bottle, of 150 c.c. capacity is fitted with a ground-in delivery tube which carries a well-fitting tap placed just above the flask, the other end of the delivery tube passing almost to the bottom of a test-tube about 20 cm. long and 2—3 cm. wide. The neck of the test-tube is fitted with a hollow stopper, through which the delivery tube is sealed; the stopper also carries a side-tube fitted with a tap. It will be seen that the test-tube is of the same construction as an ordinary Drechsel gas-washing bottle fitted with a stop-cock; in fact, the first piece of apparatus employed consisted of such a wash-bottle; it was, however, abandoned, on account of the large amount of solution required, and the smaller test-tube substituted.

In carrying out a determination, a weighed quantity of the solute is placed in the test-tube, and after both flask and tube have been half filled with solvent, the apparatus is connected together,

all ground connexions being carefully treated with rubber grease. The apparatus is now exhausted by means of a filter-pump so that all air is boiled out of both solvent and solution; to assist this boiling-out process, the flask containing the solvent may be heated gently, either with the hand or by means of a beaker of warm water; it is also advisable to sweep out the air in gusts by alternately closing and opening the tap between the flask and test-tube.

When exhaustion is complete, a process which should occupy



about half an hour, both taps are closed and the apparatus is left to itself for two or three hours to attain the ordinary temperature. The tap between the flask and test-tube should be closed during this period to prevent the forcing back of the solution into the pure solvent as a result of accidental leakage of air into the test-tube. When the ordinary temperature has been reached, the tap above the flask is gently opened, and as the vapour pressure of the solvent exceeds that of the solution, the liquid in the delivery tube is depressed below the ordinary level of the liquid in the test-tube.

This difference in height is measured either by means of a cathetometer or by having the delivery tube graduated in mm.; in either case, the observed height must be corrected for capillarity. As a check on the manometer reading, it is usually advisable to re-exhaust the apparatus without warming the solvent flask, and as the solution in the test-tube will remain practically unchanged in volume, a second pressure-reading almost identical with the first should be obtained. The temperature of the room is noted at the same time as the manometer reading is taken, and air is then admitted to the apparatus by gently raising the tap above the flask out of its seat, care being taken to prevent a violent inrush of air; the effect of capillarity is now noted, after which the test-tube is removed and weighed, and the mass of the solution so determined. If the solution is a concentrated one, its density should also be measured; in the case of dilute solutions, the density may be considered as equal to that of the solvent.

The molecular weight of the solute is calculated from the usual formula for the lowering of the vapour pressure,

$$M = \frac{P'Sm}{(P-P')s},$$

where M and m are the molecular weights of the solute and solvent, S and s their weights in grams, P the vapour pressure of the pure solvent, and P' that of the solution. The vapour pressure of the pure solvent at the temperature of the experiment is obtained by consulting tables, interpolating, if necessary, on the assumption that the curve connecting the logarithm of the vapour pressure and the temperature is a straight line.

The results obtained with alcohol and carbon tetrachloride as solvents are shown in the following table:

Alcohol as Solvent.

Solute	S.	s.	T.	P.	H.	$P-P'$.	M.	M (true).
Benzoic acid	5·698	78	19·5	42·6	17·8	1·084	128	122
Carbamide	4·043	108	19·0	41·4	21·0	1·237	56	60
Acetamide	3·781	102	17·0	36·6	17·5	1·039	59	59

Carbon Tetrachloride as Solvent.

Naphthalene	0·784	48	15·5	73·3	13·0	1·517	118	128
Phenanthrene ...	1·072	49	19·0	87·1	14·6	1·697	168	178

The headings of the different columns have the meanings ascribed to them in the formula. Column H gives the manometer readings in mm. of the solution, the heights being corrected for capillarity.

With regard to the solvents that may be employed, water is not

suitable, both on account of its very small vapour pressure and its low molecular weight. Alcohol and carbon tetrachloride were both satisfactory, although the latter showed some tendency to dissolve the rubber grease with which the taps were coated. The solvent action of the vapour on the tap lubricant quite prevented the use of benzene, and the plan of treating the taps with syrupy phosphoric acid instead of rubber proved unsuccessful, as the taps so lubricated seemed incapable of holding a vacuum.

A point of theoretical interest might be mentioned, as it applies both to the above method and that of Menzies. The vapour in the flask and delivery tube is confined between the pure solvent in the flask and the solution in the tube, and therefore it might be concluded that its pressure would lie between the values P and P'. Further consideration will show, however, that such a state is not in equilibrium, and that distillation will take place from the high pressure to the low, that is, from the solvent to the solution, until a layer of pure solvent is obtained lying on the top of the solution in the delivery tube, under which conditions the pressure of the vapour in the flask and delivery tube will be equal to that of the pure solvent.

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CV.—*The Constitution of Carbamides. Part X. The Behaviour of Urea and of Thiourea towards Diazomethane and Diazoethane respectively. The Oxidation of Thiourea by Potassium Permanganate.*

By EMIL ALPHONSE WERNER.

IT was shown by Degner and von Pechmann (*Ber.*, 1897, **30**, 647) that urea is indifferent towards diazomethane dissolved in ether. In a recent communication (this vol., p. 1098), the author has drawn attention to the fact that the action of diazomethane as a methylating agent can be conveniently studied in alcoholic solution. It was considered desirable, therefore, to test the behaviour of urea under this condition, since the result of Degner and von Pechmann's experiment could not be reasonably accepted as final, on account of the insolubility of urea in ether.

It is now shown that even when diazomethane was generated in situ with urea dissolved in alcohol, which had been previously dried by means of diazomethane, the whole of the urea was recovered unchanged after it had remained for twenty-four hours in contact with the reagent. A similar result was obtained with diazoethane. This fact is in perfect agreement with the view that the cyclic form of the urea molecule alone obtains in a neutral solution. The reactive "amino-hydroxyl" configuration occurs only when a sufficiently strong acid or alkali is present, that is, under such conditions that a salt of the type $HN{:}C(OH)\cdot NH_2,HX$ or

$$HN{:}C(OM)\cdot NH_2,$$

as the case may be, can exist in solution (T., 1918, **113**, 86).

The case of thiourea is different. Its behaviour towards iodine, with the formation of formamidine disulphide (T., 1912, **101**, 2175), the well-known reaction with alkyl haloids, whereby thio-esters of the type $HN{:}C(SR)\cdot NH_2$ are produced, and particularly its reactions with nitrous acid (T., 1912, **101**, 2180; 1913, **103**, 1221), all go to prove that in a neutral solution thiourea must be present in two molecular forms in equilibrium, thus:

$$(a)\ HN{:}C\begin{cases}NH_2\\ |\\ S\end{cases} \rightleftharpoons HN{:}C\begin{cases}NH_2\\ SH\end{cases}(b)$$

It may be well here to point out a fact which was not shown before (Expt. VI), namely, that, in contrast with urea (T., 1917, **111**, 875), thiourea is rapidly decomposed by nitrous acid alone (at concentration $N/30$), according to the equation

$$CSN_2H_4 + HNO_2 - HSCN + N_2 + 2H_2O.$$

It is obvious that it is form (*b*) that is attacked by way of the amino-group, since the sulphur remains in its original state of combination in the decomposition product, namely, thiocyanic acid.

Convincing evidence in support of the above view is supplied by the fact that thiourea is attacked by diazomethane in alcoholic solution, thus:

$$HS\cdot C(:NH)\cdot NH_2 + CH_2N_2 = CH_3\cdot S\cdot C(:NH)\cdot NH_2 + N_2.$$

The so-called methyl*iso*thiourea * was readily isolated in the form of its picrate, which melted at 221°. The reaction proceeded slowly at first, indicating the presence of form (*b*) in small amount; as the temperature gradually rose, the velocity of the change from (*a*) to (*b*) was rapidly promoted. Since the free base is unstable,

* The term "*iso*thiourea" is commonly used with reference to its relation to the "thiocarbamide" formula, the existence of which the author does not admit under any conditions. Thiourea is "*iso*thiourea" in its reactive form in solution.

it was partly decomposed, with the production of methyl mercaptan, the odour of which was evident as soon as the reaction commenced.

Ethyl*iso*thiourea picrate, which melted at 188°, was isolated from the reaction product when diazoethane was used, the change having proceeded on lines similar to the above.

When thiourea was treated with two molecular proportions of diazomethane, the excess of the latter showed no tendency to attack the methyl*iso*thiourea formed in the first instance, a result which, taken into consideration with the indifference of urea towards diazomethane, shows that an imino-group in the form HN:C: is not methylated by the reagent. In this connexion, it is interesting to note that the system ·CO·NH·CO· is capable of methylation; thus Pechmann (*Ber.*, 1895, **28**, 855) obtained methylphthalimide, and Nierenstein (*private communication*) methylsuccinimide, from their respective parent compounds.

Oxidation of Thiourea by Potassium Permanganate.

Interesting evidence in support of the existence of the two forms of thiourea in solution is supplied by a study of its oxidation by potassium permanganate under different conditions.

It was shown (T., 1912 and 1913, *loc. cit.*) that, in the presence of a sufficiently strong acid, a salt of *iso*thiourea (*b*) was alone presented for attack, and hence formamidine disulphide was produced, thus:

$$2HN{:}C\begin{matrix}NH_2,HX\\SH\end{matrix} + O = \begin{matrix}NH_2,HX\cdot\\HN{:}C\end{matrix}\!\!-\!\!S\!-\!\!S\!-\!\!\begin{matrix}\cdot XH,H_2N\\C{:}NH\end{matrix} + H_2O$$

Since the change from (*a*) to (*b*) is likewise promoted by the presence of alkali, oxidation in the presence of the latter should proceed on similar lines. This was found to be the case, but as formamidine disulphide cannot exist in the free state, its chief product of decomposition, namely, cyanamide, was obtained. The yield was 65 per cent. of the theoretical, whilst a certain amount of cyanic acid (as NaOCN) was also formed. The mechanism of this change has yet to be fully studied, but one of the chief points to be noted is that no urea was produced under either of the above conditions.

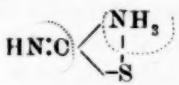
Maly (*Monatsh.*, 1890, **11**, 277) has shown that urea is formed when thiourea is oxidised by potassium permanganate in a neutral solution, and whilst nearly all of the sulphur is oxidised to sulphuric acid, it was noted that the proportion of oxygen fell short of that required by the equation

$$CSN_2H_4 + O_4 = CON_2H_4 + SO_3$$

which was given to represent the change.

A recent statement by Schmidt (*Arch. Pharm.*, 1918, **256**, 308), in referring to Maly's experiment, that thiourea is quantitatively changed into urea by potassium permanganate, cannot be upheld.* Maly distinctly stated that "the yield of urea was deceptive," and, as a matter of fact, only 5 grams of urea (theory = 12 grams) were obtained from 15·2 grams of thiourea, and no explanation was given to account for the deficiency. A repetition of Maly's experiment gave a yield of urea equal to 44·4 per cent. of the theoretical, and whilst 98·7 per cent. of the sulphur was oxidised to sulphuric acid, the amount of potassium permanganate required to decompose the whole of the thiourea was approximately nine-tenths of the theoretical for four atoms of oxygen. Whilst ammonia and a small amount of carbon dioxide were formed as by-products, a crystalline substance having the composition $C_3H_7N_5$ was isolated. This gave a silver derivative, $C_3H_5N_5Ag_2$, and the constitutional formula $HN{:}C(NH_2)\cdot C(:NH)\cdot C(NH_2){:}NH$ is provisionally suggested to explain its formation.

Since urea could not be formed by the oxidation of *iso*thiourea (form *b*), and as there was no evidence of the generation of cyanic acid during the reaction, the production of urea must, in all probability, have resulted from a direct replacement of sulphur by oxygen in the cyclic molecule (form *a*). It seems reasonable to expect that during the progress of such a change, since ammonia was one of the products, some thiourea would be decomposed, thus:



and from the union of $HN{:}C{:}$ with two formamidine residues, $HN{:}C\cdot NH_2$, derived from the oxidation of *iso*thiourea (*b*), the compound $C_3H_7N_5$ would result.

The oxidation of thiourea in neutral solution is therefore in perfect agreement with the views put forward.

Experimental.

Interaction of Thiourea and Diazomethane and Diazoethane Respectively.

Expt. I.—1·52 Grams of thiourea and 2·1 grams of nitrosomethylurea were dissolved in 30 c.c. of alcohol which had been

* A tendency to magnify unduly one change, to the exclusion of all others, has been very prevalent throughout the chemistry of urea, and, in the author's opinion, has been responsible for many of the erroneous conclusions which have been made.

previously dried * by means of diazomethane. A solution of sodium ethoxide, prepared from 0·46 gram of sodium in 20 c.c. of alcohol, was added. There was at first a feeble evolution of nitrogen, which gradually became quite vigorous as heat was developed, and after about twenty minutes the golden-yellow colour of the solution had completely disappeared.

The solution, freed from the sodium cyanate which had been precipitated (see this vol., p. 1099), was added to 30 c.c. of a cold saturated aqueous solution of picric acid, the alcohol was removed by evaporation, and the sparingly soluble picrate which had separated on cooling was collected and purified by recrystallisation from hot water. It melted at 221°, which was also the melting point of the picrate prepared from the product of the action of methyl iodide on thiourea.

Expt. II.—This was similar to the above, but 4·2 grams of nitrosomethylurea and 0·92 gram of sodium dissolved in alcohol were used (that is, 2 mols. of diazomethane generated). After the evolution of nitrogen had ceased, the residual liquid had a rich golden-yellow colour, and after twenty-four hours it was dealt with as described under Expt. I, no other picrate than that which melted at 221° being isolated from the product. Excess of diazomethane was therefore without action on methyl*iso*thiourea.

Expt. III.—1·52 Grams of thiourea and 2·35 grams of nitrosoethylurea were treated as in Expt. I. Similar phenomena were observed, and a *picrate* was obtained which melted at 188°:

0·1897 gave 33·4 c.c. N_2 at 14° and 761·5 mm. N = 20·8.

$C_3H_8N_2S,C_6H_3O_7N$ requires N = 21·08 per cent.

A picrate prepared from the product of the interaction of ethyl bromide and thiourea melted at 188°.

Experiments with urea, carried out in a similar manner, gave negative results.

Oxidation of Thiourea by Potassium Permanganate.

A. *In Neutral Solution. Expt. IV.*—To 0·076 gram of thiourea dissolved in 25 c.c. of water, 0·421 gram of potassium permanganate dissolved in 60 c.c. of water was added. After the reaction had been completed in the cold, the product was heated to 100°. The filtrate and washings gave $BaSO_4$ = 0·23 gram. Theory requires $BaSO_4$ = 0·233 gram. Hence 98·7 per cent. of the sulphur was oxidised to SO_3.

* A small quantity of a concentrated ethereal solution of diazomethane was added to pure alcohol until the solution retained a pale yellow colour after remaining for twenty-four hours.

Expt. V.—22·8 Grams of thiourea were dissolved in 400 c.c. of water, and a hot saturated solution of potassium permanganate was added (about 116 grams were required) until a slight excess of the reagent remained after the product had been heated to 100° for five minutes. The filtrate and washings from the precipitated manganese dioxide were evaporated to dryness at 100°, and the residue was extracted with hot alcohol. After concentration of the latter solution, 1·2 grams of crystals, which had separated in rosette-like conglomerates of slender, glistening prisms, were collected. They were purified from the accompanying urea by recrystallisation from hot alcohol:

0·1868 gave 0·22 CO_2 and 0·1088 H_2O. C = 32·11; H = 6·47.
0·1216 ,, 64·7 c.c. N_2 at 17° and 765·25 mm. N = 62·28.
$C_3H_7N_5$ requires C = 31·85; H = 6·19; N = 61·96 per cent.

The compound decomposed without melting at above 200°, ammonia being evolved. On addition of ammoniacal silver nitrate to the aqueous solution, a bulky, white precipitate was formed.

0·2 Gram dissolved in dilute nitric acid required 12·2 c.c. of N/10-KSCN. Ag = 65·88.
$C_3H_5N_5Ag_2$ requires Ag = 66·05 per cent.

Eight grams of nearly pure urea were obtained from the mother liquor of the above compound, equal to 44·4 per cent. of the theoretical.

B. *In Alkaline Solution. Expt. VI.*—To 0·152 gram of thiourea dissolved in 25 c.c. of water, 3 c.c. of *N*-sodium hydroxide and 0·842 gram of potassium permanganate dissolved in 100 c.c. of water were added. The oxidation was completed in a few minutes, after which the product was filtered and the precipitated manganese dioxide washed free from all soluble matter. The cyanamide present in the filtrate required 26 c.c. of *N*/10-ammoniacal silver nitrate for precipitation. Cyanamide found = 0·0546. Theory requires 0·084. Hence 65 per cent. of the theoretical amount of cyanamide was present. Sodium cyanate, the amount of which was not determined, was also present, but whether this was derived from the direct oxidation of thiourea or from cyanamide first formed has not yet been ascertained. No urea was detected in the solution.

Interaction of Thiourea and Nitrous Acid at Concentration N/30.

Expt. VII.—0·076 Gram of thiourea and 0·072 gram of sodium nitrite were dissolved in 29 c.c. of water in the nitrometer, and 1 c.c. of *N*-acetic acid was added. Evolution of nitrogen at a moderate rate commenced after a few seconds.

Vol. of N_2 (after forty minutes) = 23·6 c.c. at 17° and 767 mm. = 21·99 c.c. at *N.T.P.* Theory requires N_2 = 22·4 c.c.

Under similar conditions, urea gave no nitrogen even after remaining for three days (compare T., *loc. cit.*).

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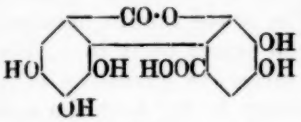
CVI.—*The Tannin of the Knopper Gall.*

By MAXIMILIAN NIERENSTEIN.

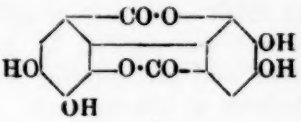
THE "Knopper Galls" (compare E. T. Connold, "Plant Galls of Great Britain," 1909, 254) or "Knoppern," as they are known in the tanning industry (compare H. R. Procter, "The Principles of Leather Manufacture," 1903, 262), are the galls produced by *Cynips calicis*, Burgsdorff, on the immature acorns of various species of oaks, principally *Quercus cerris* of the Slavonic plains, where these galls are known locally by their Slavonic and Hungarian names, "Šišarca" and "gubacs" respectively.* Their occurrence in Great Britain on *Quercus pedunculata* and also *Quercus sessiliflora* has been recorded by E. T. Connold ("British Oak Galls," 1908, 143), who refers to them also as "Gall-nuts." Löwe (*Zeitsch. anal. Chem.*, 1875, **13**, 46), who has carried out the only published investigation on knoppern tannin, described it as being identical with gallotannin. This, however, is not the case, as will be seen from the present communication. It is found that knoppern tannin yields on hydrolysis, in addition to dextrose, not gallic acid, as is the case with gallotannin, but mainly ellagic acid (II) in common with other "bloom" (ellagic acid) producing

* I am indebted for some of this information to Dr. Jan Jedlička, whom I have also to thank for the knoppern used in this investigation. Dr. Jedlička drew my attention to the ease with which the knoppern extracts deposited ellagic acid which he thought was due to the presence of a ferment in these galls, since he had succeeded in preventing the formation of ellagic acid by prolonged boiling of the extracts. I have attempted to isolate this ferment, but without success. In this connexion I may mention that I also found that emulsin has no effect on knoppern tannin, which is of interest since this ferment readily hydrolyses the tannin of *Terminalia chebula* into dextrose, luteoic acid, and ellagic acid (*Ber.*, 1910, **43**, 1268). On the other hand, I found that *Penicillium* produces ellagic acid from knoppern tannin which corresponds with the formation of gallic acid from gallotannin by *Penicillium* (compare Knudsen, *J. Biol. Chem.*, 1912, **14**, 159; Asai, *J. Coll. Sci. Tokyo*, 1918, **39**, 23).

tannins (compare A. G. Perkin and Nierenstein, T., 1905, **87**, 1412). It is also observed that methylated knoppern tannin yields on hydrolysis a mixture of partly methylated luteoic acids (I), which give on further methylation with diazomethane methyl pentamethoxyluteoate (III). The latter substance was found to be



(I.)



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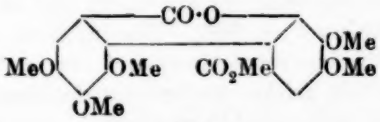

(III.)

identical with the lactone of methyl 2-hydroxy-3:4:4′:5′:6′-pentamethoxydiphenyl-6:2′-dicarboxylate (III), previously described by Herzig and Polack (*Monatsh.*, 1908, **29**, 263). From these observations it is provisionally concluded that the knoppern tannin molecule is composed of luteoic acid (I) and dextrose, the luteoic acid being predominant. Luteoic acid, which is an oxidation product of gallotannin (*Ber.*, 1908, **41**, 3015), has also been found to be the predominant component of the tannin of *Terminalia chebula* (*Ber.*, 1910, **43**, 1267). Reference ought also to be made to the presence of galloyl-*l*-leucine in the fat extracted from the knopper gall (*Zeitsch. physiol. Chem.*, 1914, **92**, 53), and the production of ellagic acid from galloylglycine by *Penicillium* (*Biochem. J.*, 1915, **9**, 240), which observations, in conjunction with the suggested configuration of knoppern tannin, may be regarded as further evidence in support of the assumption made (*Biochem. J.*, 1915, **9**, 241) that some nitrogenous galloyl derivatives serve as foodstuffs for the growing, gall-producing parasites and at the same time lead to the formation of "pathological" tannins, such as gallotannin, knoppern tannin, and the other tannins found in galls (compare Nierenstein, *Ber.*, 1910, **43**, 628; Drabble and Nierenstein, *Biochem. J.*, 1907, **2**, 96; Nierenstein and Webster, *Ber.*, 1908, **41**, 80).

Experimental.

Preparation of Knoppern Tannin.

The powdered and finely sieved knoppern were at first extracted with boiling chloroform or *s*-tetrachloroethane, so as to remove the

so-called gall-fats.* The carefully dried powder was subsequently extracted with boiling acetone. In both cases the extraction was carried out in the extraction apparatus described elsewhere (Abderhalden, "Handbuch der biochemischen Arbeitsmethoden," 1912, **6**, 149). The acetone extract was made up to 1·5 litres and the tannin precipitated with 300 c.c. of light petroleum which had been dried over calcium chloride. The crude tannin obtained in this way was purified by dissolving 50 grams of it in 1 litre of acetone and precipitating with four successive quantities of light petroleum of 100 c.c. each. It is necessary to dry both the acetone and the light petroleum over calcium chloride for some time, as otherwise the products obtained are viscid (compare also Manning and Nierenstein, this vol., p. 666). The fractions obtained weighed 26, 12, 6, and 2·5 grams respectively and were pale-coloured, amorphous products which neither melted nor decomposed when heated above 300°. They were soluble in alcohol, acetone, ethyl acetate, acetic acid, or water, but insoluble in benzene, light petroleum, or chloroform. The different solutions gave greenish-blue colorations with ferric chloride, which were particularly well-marked when the alcoholic solution was employed. This is of special interest in view of the generally accepted classification of the tannins into catechol and pyrogallol groups, which classification is based on the green and blue colorations given by these two groups respectively with ferric chloride. In this connexion it ought to be mentioned that the tannins of *Terminalia chebula* (Nierenstein, *loc. cit.*) and *Polygonum bistorta* (Stenhouse, *Phil. Mag.*, 1843, [iii], **23**, 335; Eissfeld, *Annalen*, 1854, **92**, 109; 1859, **111**, 217; Bjalobreshesky, *Pharm. J.*, 1900, **22**, 3; Jljin, *Diss.*, Petrograd, 1905, p. 38) show similar mixed colorations with ferric chloride. The aqueous solution of knoppern tannin precipitates alkaloids and gelatin, and is quantitatively adsorbed by caseinogen (compare Manning and Nierenstein, this vol., p. 667). Knoppern tannin is hygroscopic, and the determination of its elementary composition by combustion requires the same precautions as used by Geake and Nierenstein (*Ber.*, 1914, **47**, 897) in the analysis of gallotannin.

Found:

Fraction I.—C = 54·3; H = 2·1. M.W. (in acetone) = 1628, 1654, 1708. M.W. (in alcohol) = 1744, 1682, 1664.

* Preliminary investigations of the gall-fats of the knoppern seem to indicate that they are identical with the fats derived from Aleppo galls (compare Kunz-Krause and his collaborators, *Apoth. Zeit.*, 1897, **37**, 734; *Arch. Pharm.*, 1904, **237**, 256; 1907, **245**, 28). These observations refer mainly to *cyclo*gallipharic acid of the knoppern gall-fat, which had been obtained by Kunz-Krause's method. It crystallised, like his *cyclo*gallipharic acid, from light petroleum in large scales melting at 88—89°.

Fraction II.—C = 54·1; H = 2·2.

Fraction III.—C = 55·4; H = 2·4. M.W. (in acetone) = 1758, 1744, 1694. M.W. (in alcohol) = 1742, 1716, 1758, 1708.

Fraction IV.—C = 55·6; H = 2·5. M.W. (in acetone) = 1702, 1744, 1726. M.W. (in alcohol) = 1758, 1744, 1726.

For the polariscopical investigations of knoppern tannin only 0·5 per cent. solutions were used in view of the experiences of Navassarat (*Kolloid Zeitsch.*, 1913, **12**, 97) in the case of gallotannin:

Fraction I.—$[\alpha]_D^{17}$ + 31·8° (in alcohol); + 8·4° (in acetone).

Fraction IV.—$[\alpha]_D^{17}$ + 36·2° (in alcohol); + 11·8° (in acetone); + 28·6° (in water).

Hydrolysis of Knoppern Tannin.

About 0·5 gram of knoppern tannin (Fractions III and IV only were used) was dissolved in 200 c.c. of water and heated with 20 c.c. of a 5 per cent. solution of sulphuric acid for eight to twelve hours on a water-bath, a reflux condenser being used. The ellagic acid formed was collected in a Gooch crucible and washed at first with cold water, so as to remove all traces of sulphuric acid, and afterwards with alcohol and ether. The precipitate was dried at 130° and weighed as ellagic acid. (Found, C = 56·4, 55·8; H = 2·1, 2·2. Calc., C = 55·6; H = 2·0 per cent.) The filtrate was tested for dextrose by Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 915) and the dextrose was estimated volumetrically by Bertrand's method (*Bull. Soc. chim.*, 1906, [iii], **35**, 1286) as used by Nierenstein and Geake (*loc. cit.*) for the estimation of dextrose in gallotannin. In addition to this, the dextrose was also estimated polariscopically, in one case after the hydrolysis of 12·8 grams of knoppern tannin. The dextrosazone was also prepared and found to have the correct melting point. (Found, N = 15·9. Calc., N = 15·6 per cent.)

Found: Ellagic acid = 84·6, 72·4, 81·2, 78·4. Dextrose = 7·2, 6·4, 5·8, 6·7 (by Bertrand's method), 7·8 (polariscopically) per cent.

Methylated Knoppern Tannin.

The methylation (Fractions III and IV only were used) was carried out with diazomethane in ethereal suspension, and the same precautions were taken as in the case of hemlock tannin (compare Manning and Nierenstein, *loc. cit.*). The methylated knoppern tannin dissolved completely in the ether and was purified several

times by dissolving it in alcohol and precipitating with water. The methylated knoppern tannin obtained in this way was a colourless, amorphous product without any definite melting point. It was soluble in alcohol, acetone, chloroform, or *s*-tetrachloroethane, but insoluble in water or light petroleum.

Found: C = 58·8, 57·9, 58·2; H = 4·1, 4·4, 4·3; OMe = 36·9, 37·4, 37·2, 37·8. M.W. (in alcohol) = 1822, 1848, 1912. M.W. (in acetone) = 1894, 1826, 1858.

The methoxyl estimations were carried out in a Zeisel-Perkin apparatus, acetic anhydride being added. If the latter was replaced by phenol (compare Weishut, *Monatsh.*, 1913, **33**, 1165) the same result (OMe = 36·5) was obtained.

For the polariscopical investigations only 0·5 per cent. solutions were used, and the results obtained were as follows:

Found: $[\alpha]_D^{16}$ + 4·2° (in alcohol); + 6·8° (in acetone); + 16·2° (in chloroform); + 28·2° (in *s*-tetrachloroethane).

Alkali Hydrolysis of Methylated Knoppern Tannin.

Methylated knoppern tannin (about 5—10 grams) was hydrolysed by boiling with a 10 per cent. solution of alcoholic potassium hydroxide for eight hours, a reflux condenser being used. The alcohol was then evaporated and the residue extracted with boiling water, the extract being filtered from any unchanged or tarry material. On acidifying the cold solution with dilute sulphuric acid, there was obtained a bulky, colourless precipitate (Precipitate A), which was collected, washed, and dried in a desiccator. The filtrate was extracted several times with ether, which left on evaporation a tarry residue. Several attempts were made to isolate a definite disintegration product from this residue, but without success. The average yield of this residue corresponded with about 22 per cent. of the material hydrolysed. It did not reduce Fehling's solution.

Precipitate A.—This product proved to be a mixture, and it was found possible to separate it into two parts, respectively soluble and insoluble in benzene. The carefully dried substance was extracted in a Soxhlet apparatus with benzene, until a few drops of the overflow left no residue on evaporation. Five grams of the precipitate left about 2 grams in the thimble (Fraction I). The benzene solution gave on evaporation a second product (Fraction II). Both fractions were investigated separately.

Fraction I.—This product had no definite melting point (67—84°), and it was found impossible to crystallise it. The investigation of this amorphous material disclosed the following interest-

ing points, which might, perhaps, in time, prove of importance in the chemistry of knoppern tannin. It was found that the alcoholic solution gave a pronounced green coloration with ferric chloride, thus indicating (1) that it contained two hydroxyl groups in the ortho-position, and (2) that these two hydroxyl groups escaped methylation during the action of diazomethane on knoppern tannin. Attempts were also made to oxidise the alcoholic solution with silver oxide (Willstatter and Pfannenstiel, *Ber.*, 1904, **37**, 4744) or *p*-benzoquinone (A. G. Perkin, T., 1913, **103**, 661; Nierenstein, T., 1915, **107**, 860) in the hope of obtaining the corresponding *o*-quinone. These experiments, however, only gave negative results.

Found: C=56·8, 57·1; H=4·4, 4·2; OMe=27·8, 26·4, 27·3.

These analytical data indicated that Fraction I was still a mixture consisting of tetramethoxyluteoic acid (Calc., C=57·4; H=4·2; OMe=32·9 per cent.) and trimethoxyluteoic acid (Calc., C=56·3; H=3·8; OMe=25·6 per cent.), the latter being predominant.

That Fraction I was a mixture was also proved on acetylation with acetyl chloride and pyridine. The acetyl derivative was also amorphous, and decomposed on heating at about 129—135°. Only acetyl estimations by A. G. Perkin's method (T., 1905, **87**, 107) were made, which gave Ac=14·5, 13·8, 14·2 per cent., whereas the mono- and the di-acetyl derivatives require Ac=10·2 and 19·3 per cent. respectively.

On further methylation with diazomethane in ethereal solution Fraction I was entirely converted into methyl pentamethoxyluteoate (III), which crystallised from alcohol in small needles melting at 110°; this is in the vicinity of the melting point, 109—111°, given by Herzig and Polack (*loc. cit.*) for this substance. For comparison, the acid was also prepared by the method described by these authors from ellagic acid, when it was also found to melt at 110°. There was no depression of the melting point when the two preparations were mixed. (Found, C=59·1; H=5·1; OMe=46·3. $C_{20}H_{20}O_9$ requires C=59·4; H=4·9; OMe=46·1 per cent.)

Fraction II.—This fraction did not give clearly the colour reaction with ferric chloride mentioned above, but the analytical data obtained for it agreed on the whole better for tetramethoxyluteoic acid than for trimethoxyluteoic acid, although in view of the amorphous character of the product and its indefinite melting point, which was found to be 98—112°, it seems obvious that the material was not pure. (Found, C=57·8, 57·6; H=4·5, 4·7; OMe=31·7, 31·4, 31·6. $C_{18}H_{16}O_9$ requires C=57·4; H=4·2; OMe=32·9 per cent.)

It was found possible to acetylate Fraction II with acetyl chloride and pyridine, but a satisfactory product was not obtained. (Found, Ac=11·8, 12·2, 12·0. Calc., Ac=10·2 per cent.)

On further methylation with diazomethane, Fraction II was entirely converted into methyl pentamethoxyluteoate (III); small needles melting at 110° were obtained, and this melting point was not changed by admixture with Herzig and Polack's product. (Found, C=59·2; H=4·9; OMe=46·1. Calc., C=59·4; H=4·9; OMe=46·1 per cent.)

This investigation has, with many interruptions, been in progress since 1907, during which time the author has had the collaboration of Dr. D. Spence and Messrs. R. J. Thompson, J. F. Fielding, C. W. Spiers, and F. S. Wallis, for which he wishes to thank them. The author is also indebted to the Research Fund Committee of the Chemical Society and the Colston Society of the University of Bristol for grants in aid of this investigation.

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CVII.—*The Oxidation of Phenol Derivatives.*

By Cyril Norman Hinshelwood.

The observation that phenol in aqueous solution is completely and instantly oxidised by potassium permanganate whilst picric acid is very much more stable led to the examination of a number of other phenol derivatives. The mononitrophenols and the hydroxybenzoic acids are, like phenol itself, attacked by *N*/10-potassium permanganate with great rapidity. Bradshaw (*Amer. Chem. J.*, 1906, **35**, 326) carried out experiments from which he concluded that the order of attack at 0° was ortho, meta, para in acid solution and meta, ortho, para in alkaline solution. This is in accord with some older results of Dreyfus (*Compt. rend.*, 1887, **105**, 523).

Care must be exercised in drawing conclusions as to stability from the rate at which potassium permanganate is destroyed. The oxidation occurs in a series of stages of which only the first involves the breaking of the ring. Consequently, the initial rate of oxidation is the true measure of stability and the later stages are of minor importance. It is, of course, necessary to avoid complications due to the oxidation of side chains.

The method adopted for measuring the rate of oxidation was as follows. Aqueous solutions of the substances to be tested were prepared of such strength that for complete oxidation to carbon dioxide and water (and nitric acid in the case of nitro-compounds) an equal volume of $N/10$-potassium permanganate would be required. In making the calculation it was assumed that five atoms of oxygen would be yielded by the permanganate. Twenty-five c.c. of the solution were mixed with 50 c.c. of $N/10$-potassium permanganate and 10 c.c. of $N/5$-sulphuric acid in a thermostat adjusted to 25·0° and allowed to react for a measured time. The reaction was then stopped by the addition of potassium iodide and the liberated iodine titrated with $N/10$-sodium thiosulphate. As a matter of fact the potassium permanganate only yielded three atoms of oxygen, and brown oxide of manganese was always precipitated. As, however, double the amount was used which would be required if five atoms were given up, there was still an excess even when only three atoms were yielded. Moreover, the estimation of the iodine liberated gave results directly in terms of oxygen employed, independently of the actual state to which the manganese was reduced, so that complete oxidation still corresponded with a diminution of the thiosulphate titre of the mixture by 25 c.c. Two further points may be mentioned. Gooch has pointed out that acid solutions of potassium permanganate slowly lose oxygen. It was ascertained by blank determinations that no loss occurred in the longer experiments from this cause. Secondly, although the presence of any considerable amount of nitric acid is very undesirable in working with sodium thiosulphate, the concentration of that produced by the oxidation of the nitro-compounds was not sufficient to vitiate the results in any way. It was only necessary to ensure by efficient shaking that the thiosulphate did not remain in local excess during the titration.

Some results obtained with salicylic acid and with *p*-nitrophenol may be quoted first, as they serve to illustrate the complex course of the reaction and the condition for a good measure of stability.

The salicylic acid was recrystallised from water, and the *p*-nitrophenol was recrystallised twice from water and from hydrochloric acid. The pipettes and burettes were standardised, and the potassium permanganate and sodium thiosulphate solutions compared with each other daily.

The thermostat remained constant to about 0·01°.

(1) Salicylic acid.

0·4929 gram per litre.

25 c.c. Salicylic acid solution
50 c.c. $N/10$-$KMnO_4$
10 c.c. $N/5$-Sulphuric acid

Time in minutes.	Amount of oxygen used up in terms of c.c. $N/10$-$Na_2S_2O_3$
0·5	16·6
1·5	18·05
3·5	18·53
21	19·60
37	20·15
110	22·0
150	22·20
320	23·18
∞ (theor.) for complete oxidation to carbon dioxide and water.	25·0

(2) *p*-Nitrophenol.

0·496 gram per litre.

25 c.c. *p*-Nitrophenol solution
50 c.c. $N/10$-$KMnO_4$
10 c.c. $N/5$-Sulphuric acid.

Time in minutes.	Amount of oxygen used up in terms of c.c. $N/10$-$Na_2S_2O_3$.
0·55	13·2
3·0	14·75
13·5	17·2
24·5	17·5
30	17·6
38	18·13
43	18·45
54·5	19·38
61·5	20·03
75·5	20·57
∞ (theor.) for complete oxidation to carbon dioxide, nitric acid, and water.	25·0

It is clear that we have to deal in each case with consecutive reactions, the first stage of which is almost immeasurably rapid. Differences in the later stages will depend on the nature of the intermediate open-chain products, and throw no light on the stability of the original compound. This point does not seem to have received sufficient attention from Dreyfus and Bradshaw.

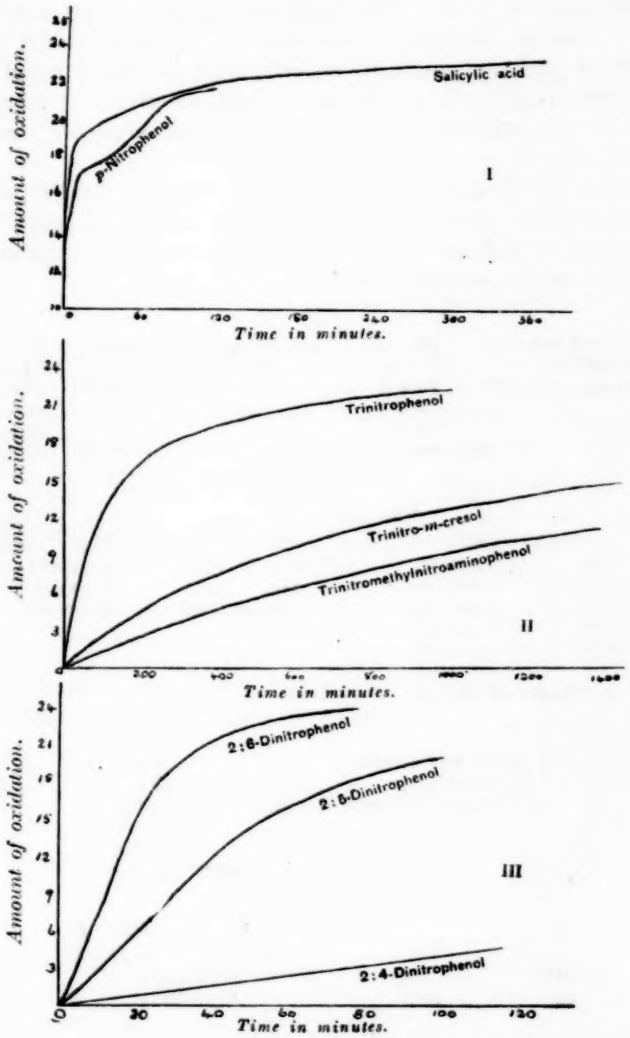
With the more highly substituted phenols quite trustworthy measurements can be made, and comparisons of stability obtained. Picric acid was taken as a standard of reference.

Picric Acid.—"Pure" picric acid was recrystallised twice from water. The solution contained 0·818 gram per litre.

(3) Picric acid 25 c.c.
$N/10$-$KMnO_4$ 50 c.c.
$N/5$-Sulphuric acid 10 c.c.

Time in minutes. t.	Amount of oxygen used up in terms of c.c. $N/10$-$Na_2S_2O_3$. x.	k (see below).
15	2·95	0·000130
26·25	4·68	0·000125
45	6·98	0·000122
83	10·50	0·000119
120	12·98	0·000120
208	16·10	0·000110
255·8	17·12	0·000105
930	21·80	—
2340	23·0	—
∞ (theor.)	25·0	—
		Mean 0·000119

In calculating k it is assumed that the permanganate yields three atoms of oxygen, so that its concentration is initially proportional



to $3/5 \times 50 = 30$. The initial concentration of the picric acid is proportional to 25, and

$$k = \frac{1}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)};$$

k being calculated for a reaction of the second order and its value

being fairly constant over the whole range, there is little evidence here of consecutive reactions. Evidently the first stage, namely, that involving the rupture of the ring, proceeds more slowly than the subsequent reactions. This accounts for the simple nature of the effect, and is confirmed by the fact that the later stages in the oxidation of *p*-nitrophenol and salicylic acid are more rapid than the corresponding stage of the picric acid reaction. k then is a measure of the stability of the picric acid molecule towards oxidation.

The effect of dilution was examined, so that less readily soluble substances might subsequently be compared with picric acid, using more dilute solutions. Incidentally, the results confirm the bimolecular nature of the change.

(4) Picric acid solution 25 c.c.
N/10-$KMnO_4$ 50 c.c.
N/5-Sulphuric acid 10 c.c.
85 c.c.
+ water 85 c.c.

$$k = \frac{2}{(30-25t)} \log_{10} \frac{5(30-x)}{6(25-x)}.$$

t.	x.	k
60	5·05	0·000120
156·5	9·65	0·000111
240	12·45	0·000111
305	13·87	0·000107
435	15·97	0·000103
Mean		0·000110

(5) Picric acid solution 25 c.c.
N/10-$KMnO_4$ 50 c.c.
N/5-Sulphuric acid 10 c.c.
85 c.c.
+ water 170 c.c.

$$k = \frac{3}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}.$$

t.	x.	k
162	7·22	0·000105
446	13·23	0·000100
581	14·98	0·000100

(6) Picric acid solution ..... 25 c.c.
N/10-$KMnO_4$ ..... 50 c.c.
N/5-sulphuric acid ..... 10 c.c.
85 c.c.
+ water 255 c.c.

$$k = \frac{4}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}.$$

t.	x.	k
213	6·85	0·0000995
563	12·50	0·0000951

The bimolecular constant diminishes somewhat with dilution.

2:4:6-*Trinitro*-m-*cresol*.—This was prepared by the thorough nitration of *m*-cresol (98 per cent.), and recrystallised three times from alcohol. A solution containing 0·7150 gram per litre was employed.

(8) 25 c.c. Trinitrocresol solution.
50 c.c. $N/10$-$KMnO_4$.
10 c.c. $N/5$-Sulphuric acid.

Time in minutes. t.	Amount of oxygen used up in terms of c.c. $N/10$-$Na_2S_2O_3$. x.	$k = \frac{1}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$.
30	0·75	—
77	1·85	0·0000149
86	2·05	0·0000149
246	5·05	0·0000146
405	7·25	0·0000141
592	9·25	0·0000137
1006	12·53	0·0000134
1355	14·28	0·0000120
∞ (theor.)	25·0	—
		Mean 0·0000141

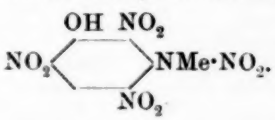
The results are completely parallel to those obtained with picric acid—the same bimolecular law and the same slight decrease in the velocity constant with time. This similarity in the dynamics of the two reactions shows, as one would expect, that a preliminary oxidation of the methyl to the carboxyl group does not disturb matters.

The ratio of the mean values of k is, then, a measure of the relative stability of the two compounds. We have:

$$\frac{k \text{ for trinitrocresol}}{k \text{ for picric acid}} = \frac{0{\cdot}0000141}{0{\cdot}000119} = 0{\cdot}118,$$

that is, trinitrocresol is only 0·118 times as reactive towards potassium permanganate as picric acid, or is 8·5 times as stable as picric acid.

2 : 4 : 6-*Trinitro*-3-*methylnitroaminophenol*,



It was thought of interest to examine this compound as an example of a very heavily substituted phenol. It was prepared by the nitration of methylaniline in the presence of excess of concentrated sulphuric acid, followed by hydrolysis of the tetranitromethylnitroamino-compound, which is one of the principal primary products. It was purified by several recrystallisations from acetone and from water, and its purity checked by acidimetric titration. A solution containing 0·757 gram per litre was employed.

(9) 25 c.c. Solution.
50 c.c. $N/10$-$KMnO_4$.
10 c.c. $N/5$-Sulphuric acid

$$k = \frac{1}{(30-25)t}\log_{10}\frac{5(30-x)}{6(25-x)}.$$

Time in minutes. t.	x.	k
180	2·55	0·00000904
351	4·43	0·00000872
372	4·60	0·00000861
1485	11·90	0·00000825
	Mean	0·00000865

$$\frac{k}{k_{\text{picric}}} = \frac{0{\cdot}00000865}{0{\cdot}000119} = 0{\cdot}0725.$$

The reactivity towards potassium permanganate is thus 0·0725 times that of picric acid, or the compound is 13·8 times as stable. Here, again, the similarity between the dynamics of this reaction and the picric acid reaction may be taken to show that the side-chain does not suffer attack before the ring is broken. (See Fig. II.)

Dinitrophenols.

In the case of three dinitrophenols curves of a somewhat different type were obtained. I am greatly indebted to Mr. Aldous, who kindly supplied me with pure specimens of the compounds used.

The solutions (0·3285 gram per litre) were of half the strength used in the previous experiments, and the potassium permanganate and acid correspondingly of half strength.

(10) 2:6-Dinitrophenol.

50 c.c. Dinitrophenol solution.
100 c.c. $N/20$-$KMnO_4$.
20 c.c. $N/10$-Sulphuric acid.

Time in minutes. t.	Amount of oxygen used up in terms of c.c. $N/10$-$Na_2S_2O_3$. x.	x/t.
5	3·40	0·680
7·7	5·35	0·693
10	7·05	0·705
15·5	11·00	0·709
18·3	13·17	0·720
20	14·48	0·724
27·3	17·70	—
44·6	21·5	—
330	24·25	—
∞ (theor.) for complete oxidation to carbon dioxide, nitric acid, and water.	25·0	—

(11) 2:4-Dinitrophenol.

50 c.c. Dinitrophenol solution.
100 c.c. $N/20$-$KMnO_4$.
20 c.c. $N/10$-Sulphuric acid.

Time in minutes. t.	Amount of oxygen used up in terms of c.c. $N/10$-$Na_2S_2O_3$. x.	x/t.
11·3	0·26	—
150	5·60	0·0373
206	8·0	0·0388
307	11·60	0·0378
422	15·86	—
∞	25·0	—

(12) 2 : 5-Dinitrophenol.

50 c.c. Dinitrophenol solution.
100 c.c. $N/20$-$KMnO_4$.
20 c.c. $N/10$-Sulphuric acid.

Time in minutes.	Oxygen used up in terms of c.c. $N/20$-$Na_2S_2O_3$.	x/t.
16	4·67	0·292
23·5	6·67	0·284
31	9·12	0·294
41	12·45	0·304
55	14·57	0·265
68	16·87	—
87	19·00	—
155	21·79	—
∞	25·0	—

The form of the curves is quite different from that obtained with picric acid. The reactions are autocatalytic, a point which will be referred to again later. The approximate constancy of x/t over a considerable range has little theoretical bearing, but enables the initial velocity to be calculated in each case.

Initial rate of oxidation in c.c. per minute for 2 : 6-dinitrophenol = 0·705.

Initial rate of oxidation in c.c. per minute for 2 : 4-dinitrophenol = 0·0379.

Initial rate of oxidation in c.c. per minute for 2 : 5-dinitrophenol = 0·294.

The corresponding initial rate for picric acid in the same units may be found by evaluating dx/dt for $t=0$ from the expression in Expt. 4 (half strength picric acid):

$$\frac{2}{(30-25)t}\log_{10}\frac{5(30-x)}{6(25-x)} = k_2 = 0{\cdot}000110,$$

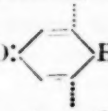
whence

$$\left(\frac{dx}{dt}\right)_0 = 0{\cdot}0950.$$

Approximate experiments further give a lower limit for the initial rates in the case of phenol and some mono-derivatives. The results are combined in the table below:

Compound.	Relative rate of oxidation.	Relative stability of ring.
Phenol, Salicylic acid	>500	<0·002
o-Nitrophenol, *m*-Nitrophenol, *p*-Nitrophenol	>250	<0·004
2 : 6-Dinitrophenol	7·4	0·135
2 : 4-Dinitrophenol	0·40	2·50
2 : 5-Dinitrophenol	3·09	0·324
Picric acid	1·00	1·00
2 : 4 : 6-Trinitro-*m*-cresol	0·118	8·5
Trinitromethylnitroaminophenol	0·073	13·8

Taking into consideration the nature of the curves, it is thought that these figures give a true measure of the relative stability of the ring in the various compounds. If the initial velocity were in any case that due to the formation of another aromatic derivative indications of consecutive reactions would be found. In the only cases where these were found, namely, phenol and its mono-derivatives, the first rapid change was far too profound to be other than a complete decomposition of the aromatic nucleus.

In general, whilst phenol and its mononitro- and carboxy-derivatives are extraordinarily unstable towards potassium permanganate, the more heavily substituted compounds have acquired considerable stability. There is no definite connexion between rate of oxidation and degree of ionisation. The instability of phenol renders a true aromatic constitution improbable. It may be provisionally suggested that the reactivity is due to the production of the tautomeric keto-form,  , or, in accordance with the principle of Baly and Stewart, to the actual oscillation between this and the normal form. Heavy substitution might be expected to inhibit tautomerisation and to depress the reactivity. On this view the autocatalytic reaction in the case of the dinitrophenols could be simply explained. The yellow solutions of these compounds are decolorised by moderate amounts of sulphuric acid. This may well be due to the repression of a quinonoid keto-form. As oxidation proceeds sulphuric acid enters into the reaction, and the keto-form can reappear. Hence the acceleration.

In conclusion, I wish to thank Mr. D. H. Nagel, M.A., for the interest he has taken in these experiments.

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CVIII.—*Chloropicrin. Part I.*

By JOHN ADDYMAN GARDNER and FRANCIS WILLIAM FOX.

WHEN commercial chloropicrin, purified by distillation in a current of steam and dried over calcium chloride until it no longer restores the blue colour to anhydrous copper sulphate, is distilled under atmospheric pressure, it boils at about 112°, and a small amount of a yellowish-red gas, recalling in appearance diluted nitrous fumes,

is always evolved which is seen in the atmosphere of the condenser and receiver. After several redistillations the distillate and the chloropicrin remaining in the flask were found on analysis to contain the same percentage of chlorine.

No mention of this phenomenon could be found in the literature. Stenhouse (*Annalen*, 1848, **66**, 241) states that the substance distils unchanged at 120°, and can be heated to 150° without undergoing decomposition, but if the vapour is passed through a heated glass flask, at a temperature below red heat, it decomposes completely, chlorine and nitric oxide being evolved and a quantity of perchloroethane being deposited in the cooler part of the flask. Hofmann (*Annalen*, 1866, **139**, 111) gives the boiling point 112°, and Thorpe (T., 1880, **37**, 198) 111·91°, but neither observer mentions any decomposition. Cossa (*Gazzetta*, 1872, **2**, 181) gives the boiling point 112·8°, and states that the substance explodes when rapidly heated or when the vapour is led into a red-hot tube. Levy and Jedlicka (*Annalen*, 1888, **249**, 86) state that bromopicrin explodes on distillation under the ordinary pressure, giving red fumes, but that it can be distilled unchanged under diminished pressure. In the article on chloropicrin in Wurtz's "Dictionnaire de Chimie," the writer states that "elle bout à 120°; à 112° (Hofmann): elle supporte une temperature de 150° sans se décomposer; surchauffée sa vapeur fait une violente explosion."

It seemed of interest, therefore, to submit the phenomenon to closer investigation.

When chloropicrin was caused to explode by heat or otherwise, a strong odour of carbonyl chloride was always noticed. This fact, together with the constancy of composition after boiling, suggested that chloropicrin at its boiling point slowly decomposes into carbonyl chloride and nitrosyl chloride:

$$CCl_3{\cdot}NO_2 = COCl_2 + NOCl.$$

This was found to be the case, and 200 c.c. of that liquid, kept very gently boiling, decomposed at the rate of about 2 c.c. per day.

This observation is of interest for a variety of reasons. It throws light on the rather divergent statements that have been made on the physiological activity of chloropicrin. In making experiments on this subject, the mixture of chloropicrin vapour and air to be tested on animals should be made either by atomising the liquid into the air or by evaporating at a low temperature; if the mixture were made by boiling the chloropicrin, or by bursting a bomb by any means, the atmosphere produced would contain chloropicrin vapour more or less contaminated with carbonyl chloride and nitrosyl chloride, and if the air were damp perhaps also nitrous fumes, so that a mixed result would be obtained.

It also throws light on many of the chemical reactions of chloropicrin, which is a very reactive substance. It has already been pointed out by Frankland, Challenger, and Nicholls (this vol., p. 159) that under some conditions chloropicrin is reduced quantitatively to methylamine, but under others to ammonia, etc. Obviously in the first case it is reduced as such, and in the latter the decomposition products are reduced.

There are many other reactions in which chloropicrin behaves as an oxidising agent. In some it appears to react as a nitro-compound; for instance, it can be used to replace nitrobenzene in Skraup's method of preparing quinoline, in others the results can be explained as due to the decomposition products. We hope shortly to have the honour of bringing before the Society a detailed account of some of these reactions.

This decomposition may also account for the varied yields obtained by different observers in the production of chloropicrin by the action of bleaching powder on picric acid. By proper attention to the proportions of the reagents and the conditions of reaction yields of 180—190 per cent. of the picric acid used can easily be obtained on a technical scale,* but if the optimum conditions are not strictly adhered to the yield may easily sink to 130 per cent., or even to 114 as given originally by Hofmann, or less.

Experimental.

Chloropicrin, in quantities of about 200 c.c., was boiled, on a sand-bath, in a 300 c.c. flask with a long neck and provided with a long reflux condenser. The end of the condenser was connected to a series of wash-bottles containing the reagents for absorbing the

* The proportions found to be best for obtaining yields of about 180 per cent. were 10 parts of picric acid to 100 parts of bleaching powder. The exact proportion, however, depends on the quality of the latter. The material used generally contained about 33 per cent. of available chlorine. The method adopted was to carry out a trial distillation with the above proportions. If it was found in the trial distillation that the effluent was at all yellow the amount of picric acid was lessened. If it was found that there was any tendency to frothing, a little extra was added. This was found to be a much more satisfactory method of work than attempting to estimate each batch of bleaching powder. The best conditions for the reaction are for the bleaching liquor to be about 30°, when on the addition of solid picric acid the temperature very rapidly rises to distilling point and steam is only used in the final stage of the reaction to carry over the last traces of chloropicrin. Contrary to statements frequently made, no artificial means of evading frothing is of any practical use. Once frothing commences badly, the yield steadily diminishes. On the large scale, the only way of destroying froth is to add a further small quantity of solid picric acid, a somewhat unpleasant, not to say dangerous operation.

products of decomposition. The various parts of the apparatus were joined either by ground-glass joints or by sealing in the blow-pipe.

In the earlier experiments the wash-bottles were charged with 40—50 per cent. potassium hydroxide solution to absorb the whole of the products of decomposition. At the end of an experimental period the contents of the bottles were diluted to definite volume and estimations were made of the carbonate, nitrite, and chloride present. The method did not prove quite satisfactory, as the connecting tubes were apt to become clogged with crystalline matter deposited from the concentrated alkaline solution. It also proved difficult to obtain complete absorption of the carbonyl chloride. The latter difficulty was overcome by charging the last bottle with $N/2$-alcoholic potassium hydroxide. Owing to the large bulks of concentrated alkali hydroxide required, and the long duration of the experiments, it proved troublesome to make very exact corrections for the chlorides and carbonates contained in the original potassium hydroxide.

In two experiments the ratio $CO_2:NO_2:Cl$ was found to be 1:1·003:2·14 and 1:0·993:2·42 respectively. The theoretical ratio is 1:1·046:2·42.

In subsequent experiments the constituents of the mixture were absorbed separately.

The first wash-bottle was charged with concentrated sulphuric acid, which absorbed the nitrosyl chloride, producing hydrogen chloride and nitrosylsulphuric acid,

$$NOCl + SO_2(OH)_2 = SO_2{\cdot}OH{\cdot}ONO + HCl.$$

The mixture of hydrogen chloride and carbonyl chloride was then passed into bottles containing either benzene or toluene to absorb the carbonyl chloride. The hydrogen chloride was either allowed to escape, or in some experiments was collected in copper sulphate solution.

Examination of the Sulphuric Acid Liquor.

The contents of the first bottle had all the properties of a solution of nitrosylsulphuric acid in concentrated sulphuric acid. It did not, however, crystallise on long keeping in the ice-chest, even when the nitrosyl chloride had been passed through up to the limits of the capacity of the acid for efficient absorption. The liquor was therefore submitted to fractional distillation under diminished pressure. It was not possible to obtain a complete separation of the sulphuric acid from the nitrosylsulphuric acid, since some of the latter passed over even in the first runnings which, on keeping in the air for a short time, became distinctly blue. When about half

the acid had passed over, the sides of the receiver began to be coated with the well-known chamber crystals. On further distillation solid deposited in the condensing tube, the liquid in the receiver crystallised, and the residue in the distilling flask solidified on cooling.

This crystalline matter was purified, so far as possible, from free sulphuric acid by keeping it for many days on porous tile over sulphuric acid in a desiccator, and occasionally scraping on to fresh tile. In this way a quantity of approximately pure nitrosylsulphuric acid was obtained as a white, crystalline mass, which began to soften at about 30° with evolution of vapour. The crystals dissolved in a trace of water to a blue liquid, were readily soluble in concentrated sulphuric acid, and on dilution with much water gave a solution of sulphuric and nitric acid. The preparation contained no trace of chlorine.

A specimen was analysed by estimation of sulphuric acid after dissolving in water, and by titration of the solution in concentrated sulphuric acid into permanganate (Found, $SO_3 = 63{\cdot}86$, oxygen required $= 11{\cdot}93$; Calc., $SO_3 = 63{\cdot}01$; oxygen required $= 12{\cdot}59$ per cent.).

Examination of the Benzene or Toluene Solutions.

A toluene solution (114 c.c.), containing carbonyl chloride liberated in four days, was shaken with 150 c.c. of 40 per cent. potassium hydroxide solution in a closed bottle in the shaking machine for six hours. The alkaline layer was then made up to 250 c.c. Estimations of chloride and carbonate were made in this, and also in a control sample of potassium hydroxide, similarly treated.

(1) 25 c.c. gave 2·6954 AgCl and 0·4487 CO_2.
(2) 25 c.c. ,, 2·6911 AgCl.
(3) 26 c.c. control gave 0·0397 AgCl and 0·0372 CO_2.

Ratio $Cl : CO_2 = 1 : 0{\cdot}6266$.
Theory for $CoCl_2 = 1 : 0{\cdot}6205$.

This toluene solution, from the rate of decomposition given below, should have contained between 8·4 and 11·2 grams of carbonyl chloride. It actually contained from the above analysis 9·16 grams.

In another experiment about 500 c.c. of benzene, containing the carbonyl chloride produced in forty-one days, were boiled in a flask with a reflux condenser, the upper end of which was connected to a worm condenser and receiver, both cooled by a freezing mixture of ice and salt, when between 7 and 8 c.c. of liquid carbonyl chloride, boiling at 8°, were obtained.

Much carbonyl chloride escaped condensation under these conditions, and a considerable amount remained in the benzene. The residual solution was shaken with concentrated aqueous ammonia and the aqueous layer evaporated to dryness. The crystallised residue was mainly ammonium chloride, but a trace of carbamide was isolated from it in the usual manner, and identified by its crystalline form, the biuret test, and the evolution of ammonia on treatment with soya-bean urease.

For the further identification of the carbonyl chloride it was converted into benzophenone by the Friedel and Crafts method. For this purpose about 250 c.c. of benzene, containing the carbonyl chloride evolved in seven to eight days, were used.

The benzophenone crystallised from alcohol in the usual characteristic form, and melted at 48·5—49°. A mixture with a specimen from another source showed no change in melting point. The yield was about 62 per cent. of the theoretical, and was similar in order to that recorded by Friedel and Crafts (*Ber.*, 1877, **10**, 1856).

Dimethyl-*p*-aminobenzoic acid was also obtained, with other products, in needle-like crystals melting at 235°, by heating a toluene solution with dimethylaniline in a closed flask at 130° for several hours, and then distilling off the toluene in a current of steam.

Examination of the Chloropicrin left after Prolonged Heating.

This was yellow, and completely volatile in steam, leaving no residue. On distillation the following fractions were obtained: up to 103°, 3 grams; 103—108°, 5·2 grams; 108—112°, 278·7 grams; residue in flask, 3·8 grams. It was evidently unchanged chloropicrin.

The chloropicrin, after distillation in a current of steam, contained some nitrous fumes in solution, which were given off at the beginning of distillation and coloured the first fraction brown. These were easily displaced by a current of air.

Fraction 3 was found to contain Cl = 64·79, and two specimens of the commercial chloropicrin used 64·82 and 64·92 respectively. CO_2NCl_3 requires Cl = 64·71 per cent.

Rate of Decomposition.

Chloropicrin (200 c.c.) was gently boiled for sixty-eight days, and 58 c.c. remained at the end. It decomposed therefore at the rate of 2·088 c.c. or 3·487 grams per day, and produced 2·099 grams of carbonyl chloride per day.

In another experiment in which the chloropicrin was kept rapidly

boiling, 64·6 grams of carbonyl chloride, determined from the increase in weight of the toluene wash-bottles, were obtained in twenty-three days, a rate of decomposition giving 2·8 grams per day.

In order to ascertain whether this decomposition could be attributed to traces of moisture, the chloropicrin, which had been dried over calcium chloride and gave no reaction with anhydrous copper sulphate, was allowed to remain for several days with a large excess of phosphoric oxide. It was then transferred to the carefully dried apparatus and heated as described. Decomposition took place, and 8 grams of carbonyl chloride were obtained in ninety-one hours, a rate of decomposition giving 2·097 grams per day, and of much the same order as before. The residual chloropicrin was found to contain Cl = 64·65 per cent.

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CIX.—*The Temperature of Critical Solution of a Ternary Mixture as a Criterion of Purity of* n-*Butyl Alcohol. The Preparation of Pure* n-*Butyl Alcohol.*

By KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES.

SINCE the introduction of the fermentation process, *n*-butyl alcohol prepared from starch has become a common industrial product which will certainly find a use in chemical industry and not improbably as a solvent.

We have examined some of its solubility relations with the object of finding in the temperature of critical solution ("c.s.t.") with other media a rapid and certain method of following the course of a fractionation by which butyl alcohol is being purified, or of detecting the presence of impurity in a specimen of butyl alcohol. It was pointed out in a previous paper (this vol., p. 1055), on a similar use of this method for toluene, that different impurities both present together in the liquid under investigation may have an opposite effect on the c.s.t. as on other physical properties. Usually, however, the c.s.t. of a number of fractions

into which the liquid has been divided by distillation will reveal the true condition of the liquid.

The solubility relations with water of the three isomerides of *n*-butyl alcohol have been studied by Alexéev (*Ann. Phys. Chem.*, 1886, [iii], **28**, 305) and Timmermans (*Zeitsch. physikal. Chem.*, 1907, **58**, 129).

tert.-Butyl alcohol is miscible with water at the ordinary temperature, whilst the solubility curve of *iso*butyl alcohol has a c.s.t. at 130° (Alexéev), and *sec.*-butyl alcohol one at 113·7° (Alexéev, Timmermans). Both curves show a maximum of mutual insolubility in the neighbourhood of 50°. The solubility curve of *n*-butyl alcohol has not been followed up to the c.s.t., which will be well above 150°, but it shows a similar maximum of insolubility at about 50°.

As a criterion of purity, the binary c.s.t. with water would not only be at an inconvenient temperature and pressure, but useless for detecting the commonest impurity, namely, water. No other binary mixture seems available, for although ethyl alcohol forms a binary with petroleum, which has found a similar application in Crismer's hands, and methyl alcohol with carbon disulphide, the higher alcohols are completely miscible with these liquids. A ternary mixture was therefore sought.

A 14 per cent. (13·994 grams per 100 grams of solution) solution of hydrochloric acid was chosen, as both very convenient for our purpose and sufficiently sensitive; it gives an upper c.s.t. at 43·55° and a lower at 9·6° with *n*-butyl alcohol.

n-Butyl alcohol is completely miscible with concentrated hydrochloric acid (20 per cent.) at the ordinary temperature (Lieben and Rossi, *Annalen*, 1871, **158**, 137). The presence of hydrochloric acid causes a contraction of the solubility ring of the system butyl alcohol–water, in the same way as does ethyl alcohol that of the system methyl ethyl ketone–water (Bruni, *Atti R. Accad. Lincei*, 1899, [v], **8**, 141).

Fig. 1 represents the change in the system *n*-butyl alcohol–water when hydrogen chloride is introduced. The solubility ring, KK', of water and butyl alcohol has, as yet, been followed over only a small section of the lateral portions; the intervention of the solid–liquid curve, sl, prevents the realisation of the lower c.s.t. K'. When hydrogen chloride is present, the ring contracts; L', the lower c.s.t., appears above the ice line, and L, the upper, is now at a lower temperature. As the concentration of the hydrogen chloride increases, the ring further contracts until, finally, miscibility is complete.

Aqueous sulphuric and nitric acids give upper ternary c.s.t.'s, but no lower c.s.t.'s were observed:

Sulphuric acid (24 per cent.) gave a c.s.t. at 8°, nitric acid (35 per cent.) at 5°.

Sulphuric acid (20 per cent.) gave a c.s.t. at 80°, nitric acid (31 per cent.) at 37°.

The method of determining the c.s.t., and the apparatus employed, have been fully described in an earlier paper (*loc. cit.*).

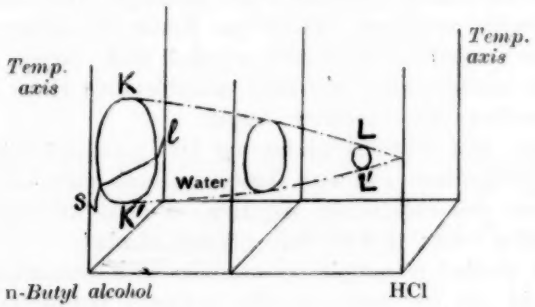
The quantities of the acid solution and butyl alcohol which gave very vividly the critical phenomena are:

Acid solution, 1 c.c.; butyl alcohol, 0·4958 c.c.

Pipettes of the type used for toluene were constructed and carefully calibrated to deliver these quantities with that exactness which we have shown (*loc. cit.*) to be so necessary.

The n-*Butyl Alcohol*.—In order to prepare a pure *n*-butyl

FIG. 1.



alcohol, several specimens from various sources have been examined. The untreated alcohols gave c.s.t.'s with the standard aqueous hydrochloric acid varying between such wide limits as an upper c.s.t. of 84° and complete miscibility, whereas pure butyl alcohol gives the value 43·55°.

Most of these crude alcohols, after treatment with ordinary chemical reagents—dilute acids to remove bases, sodium hydrogen sulphite to remove aldehydes and ketones, and boiling sodium hydroxide to decompose esters—and subsequent distillation, were found capable of giving a large percentage of material, the various fractions of which, on redistillation, gave the same c.s.t. about 43°. Some of the material, however, which was homogeneous so far as could be tested by distillation, gave c.s.t.'s varying widely from this value; as one example, the c.s.t. was about 50°, and as another about 60°.

As examples of the behaviour of these crude butyl alcohols on distillation, the following may be cited:

(1) A crude specimen (1000 c.c.) had an initial c.s.t. of 44·8°. After drying with potassium carbonate, the c.s.t. was reduced to 37·8°. On distillation through an eight-bulb still-head, the main fraction of 550 c.c., boiling at 116·5°, gave a c.s.t. of 46·8°.

After chemical treatment and redistillation, a considerable quantity of homogeneous material could be obtained from this main fraction (as well as from other specimens which had been similarly treated), the c.s.t. of which was 43—44°.

An alcohol (1000 c.c.) from another source, which was remarkable as being initially completely miscible with the standard hydrochloric acid, on mere distillation through an eight-column Young and Thomas dephlegmator furnished 750 c.c. of a homogeneous material giving a c.s.t. of 43°.

Two other examples may be mentioned of specimens which give after a similar treatment quite different values of the c.s.t.

Table I shows a record of fractionation of a specimen giving an initial c.s.t. of 66·7°.

TABLE I.

Temperature.	Volume of distillate.	Critical point.	Temperature.	Volume of distillate.	Critical point.
116·0°	10 c.c.	63·1°	116·3°	10 c.c.	61·5°
116·2	10 ,,	61·7	116·4	10 ,,	61·7
116·3	10 ,,	59·8	116·4	10 ,,	62·4
			116·5	10 ,,	64·6
			Residue.	7 ,,	above 90

Treatment with chemical reagents left the value of the c.s.t. unaltered.

The fractionation of another specimen, which gave after fractionation a homogeneous material with a c.s.t. of about 50°, is cited below (table II).

One was thus unable, in the absence of a pure synthetic alcohol, to decide definitely whether the homogeneous material, giving a c.s.t. of 43°, contained an impurity impossible to remove by distillation, which lowered the c.s.t., or whether the homogeneous material, giving a much higher c.s.t., contained impurities such as paraffins of similar boiling point, impossible to remove by distillation or chemical treatment, which raised the c.s.t.

It has been no simple matter to find a derivative of *n*-butyl alcohol which would provide a means of obtaining the pure substance. The derivative should preferably be a crystalline solid, into which the alcohol could be readily converted, and from which

as readily recovered without chemical change of the alcohol. The sodium salt of butyl salicylate meets these conditions.

A large quantity of the alcohol, the fractionation of which is shown in the table (table II), was converted into the salicylate;

TABLE II.

Fraction.	Volume.	Critical solution point.
1	40 c.c.	57·0°
2	252 „	50·0
3	415 „	49·3
4	295 „	49·0
5	28 „	50·05

the sodium salt is prepared by dropping the ester into a slight excess of 10 per cent. sodium hydroxide which is being vigorously stirred. The sodium salt crystallises out immediately; it is collected and freed from alherent liquor by pressure. The salt is reconverted into the ester by slowly adding both 10 per cent. hydrochloric acid and the solid salt to a large volume of cooled water which is being stirred. This process is repeated with the recovered ester. The ester is then hydrolysed by aqueous sodium hydroxide, and the butyl alcohol, saturated with water, is dried with potassium carbonate and distilled. Overheating, which would in itself lead to contamination, was avoided by using an oil-bath in this and other distillations. The table shows the values of the c.s.t.'s of the fractions in the final distillation.

TABLE III.

Fraction.	Weight of fraction. Grams.	Critical solution point.
1	10	43·7°
2	27	43·55
3	27	43·55
4	30	43·5
5	20	43·5
Residue	about 5	—

It is seen that the material is now remarkably homogeneous. This *n*-butyl alcohol, which gives an upper c.s.t. at 43·55° and a lower c.s.t. at 9·6° with 13·994 per cent. hydrochloric acid, has $D^{14\cdot4}_{14\cdot4}$ 0·81617.

Relation between the Concentration of Hydrochloric Acid and the Ternary Critical Solution Temperatures observed with n-*Butyl Alcohol.*

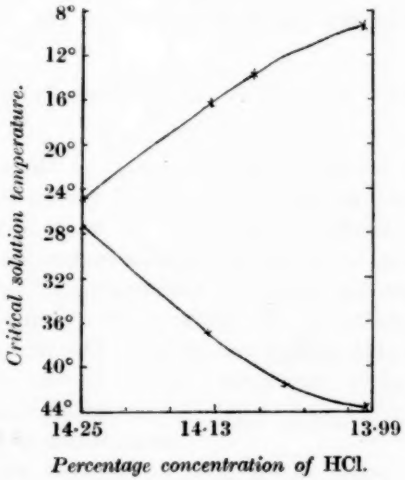
The c.s.t. is extremely sensitive to change in the concentration of the hydrogen chloride. Hydrochloric acid solutions of various

strengths were made up, and a definite volume (1 c.c.) was added to a definite volume of *n*-butyl alcohol (0·4958 c.c.) in the experimental tube. The table shows the experimental values, and Fig. 2 the curves constructed from them.

TABLE IV.

Concentration of acid. (Grams in 100 grams of solution.)	Critical solution points. Upper.	Lower.
13·994	43·55°	9·6°
14·068	41·8	12·1
14·133	36·8	16·3
14·248	27·4	25·0

FIG. 2.



So small a change in the concentration of the hydrochloric acid as 0·254 per cent. alters the upper c.s.t. by 16·15°, and the lower by 15·4°. This great sensitiveness would afford a means of ascertaining whether two solutions of hydrochloric acid within a small range were of accurately identical concentration.

The measurement of the concentration of the hydrochloric acid solution has required exceptional care. As the most accurate process, a determination was chosen based on the measurements of the iodine (by $N/20$-thiosulphate, and starch indicator), set free from a mixture of potassium iodide and iodate, in which the amount of iodate is very accurately known. (Fuller details of the procedure will appear, it is hoped, in another place.) This method has been fully tested, and the accuracy with which

the solution of hydrochloric acid has been measured is represented by the number 14·248±0·001 per cent. This mean error corresponds with a difference of 0·05° in the c.s.t. of the system *n*-butyl alcohol–water–hydrochloric acid. This particular solution of hydrochloric acid was used throughout the experiments on the purification of *n*-butyl alcohol.

Obviously, in preparing an aqueous hydrochloric acid for the purpose of following the purification of *n*-butyl alcohol, the concentration of the hydrochloric acid used need not be known with such accuracy. With the ordinary volumetric solutions, accurately standardised, and by using standard burettes, the concentration of the hydrochloric acid can be ascertained as 14·0±0·02 per cent., and by a gravimetric analysis as 14·0±0·005 per cent. The divergence in the c.s.t. corresponding with this mean error will amount to 1° in the one and to 0·25° in the other.

The Sensitiveness of the Critical Solution Temperature to Impurities.

Water.—Water is one of the components of the system, and its effect as an impurity in the *n*-butyl alcohol is seen from table V to be comparatively slight; 1 per cent. of water raises the upper c.s.t. by 1°. Here, as in all these experiments on the effects of impurities, the concentration of the hydrogen chloride remains constant, the composition of the system only altering in the relative proportions of *n*-butyl alcohol and water. The immensely different effect produced when the concentration of the *n*-butyl alcohol remains constant, while the ratio $\frac{\text{concentration of HCl}}{\text{concentration of } H_2O}$ is varied, is seen from the results on the relation between the concentration of the hydrochloric acid and the c.s.t., when a change of 0·25 per cent. leads to a fall or rise in the c.s.t. of 16°.

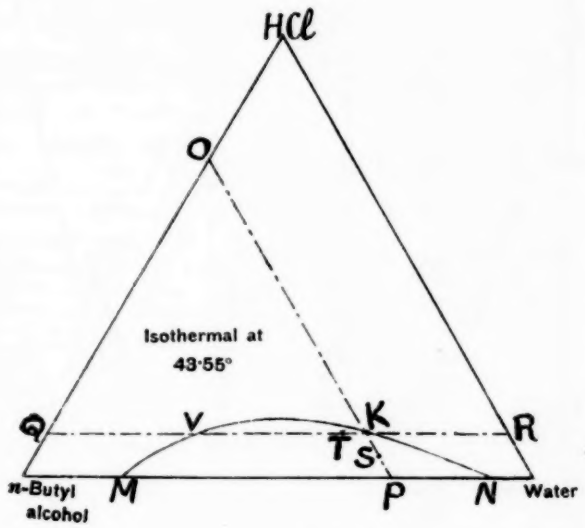
An explanation of this divergence is forthcoming from a consideration of the isothermal diagram at 43·55°.

In Fig. 3, *M* (80 per cent. of butyl alcohol) and *N* (8 per cent. of butyl alcohol) represent, roughly, the composition of a saturated solution of water in *n*-butyl alcohol and of alcohol in water at this temperature. *K* represents the composition of the system at the ternary c.s.t. at 43·55°. (HCl = 10·15; *n*-butyl alcohol = 27·45; water = 62·4 per cent.)

From these results, it appears that the binodal curve has the general form shown—a curve with a very flat top. The line *OKP* represents the composition of the system with constant concentration of *n*-butyl alcohol, and the line *QKR* the composition of

the system with constant concentration of hydrochloric acid. From K, movement along KSP, that is, decrease in the concentration of the hydrochloric acid, with a corresponding increase in the concentration of water, the concentration of the alcohol being constant, brings the system into the heterogeneous region; by movement along KTQ, that is, decrease in the concentration of water, with a corresponding increase in the concentration of the alcohol, the concentration of the hydrochloric acid being constant, the system is brought again into the heterogeneous region, but at

FIG. 3.



no point is it far removed from the binodal curve, which it again cuts at V.

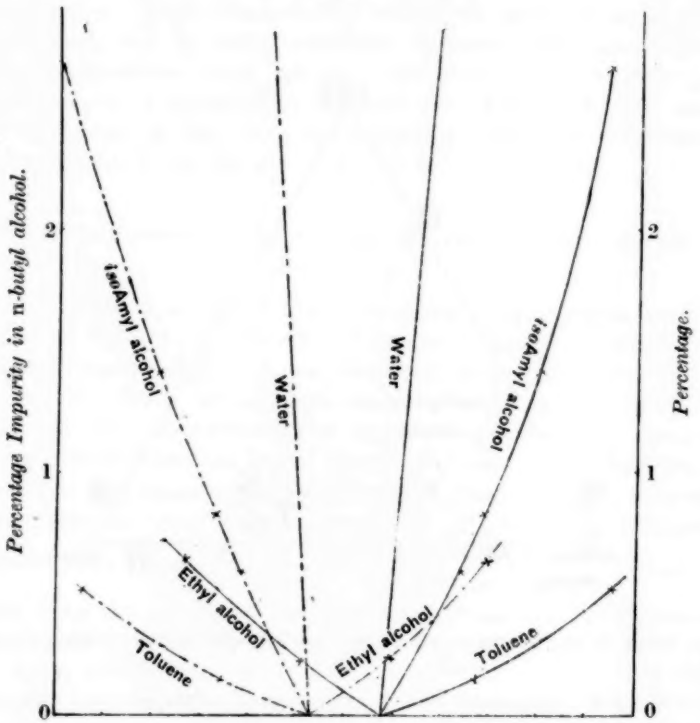
Let KT represent a 1 per cent. change in the ratio $\frac{n\text{-butyl alcohol}}{\text{water}}$, the concentration of the hydrochloric acid being constant, then KS, which equals KT, represents a 1 per cent. change in the ratio $\frac{\text{hydrochloric acid}}{\text{water}}$, the concentration of the alcohol being constant. S is obviously very much further removed from the binodal surface than T. Hence, as a result of the form of the binodal curves, a far larger change of temperature would be required to bring the system at S on to a binodal curve than the system at T on to a curve.

The results obtained with the other substances, namely, toluene,

ethyl alcohol, and amyl alcohol, which have been tested, appear in table V and Fig. 4.

The c.s.t. is extremely sensitive to the presence of such a substance as toluene, the solubility of which in water so greatly differs from that of *n*-butyl alcohol. One per cent. of toluene in the butyl alcohol raises the upper and depresses the lower c.s.t. by 19°. Paraffin, which is less soluble, has a still greater effect.

FIG. 4.



Upper critical solution temperatures.

30° 32° 34° 36° 38° 40° 42° 44° 46° 48° 50° 52° 54°

Lower critical solution temperatures.

−1° 1° 3° 5° 7° 9° 11° 13° 15° 17° 19° 21° 23°

Discontinuous curves represent the effect of impurity on the lower c.s.t.
Continuous curves represent the effects on the upper c.s.t.

The c.s.t. is thoroughly sensitive to the presence of homologues. One per cent. of ethyl alcohol lowers the upper c.s.t. by 11°, and 1 per cent. of amyl alcohol raises the upper c.s.t. by 5°, correspond-

ing alterations being observed in the lower c.s.t. Rough experiments with *n*-propyl, *iso*butyl, and *sec.*-butyl alcohols show a less, but still an appreciable, effect. One per cent. of *n*-propyl alcohol lowers the c.s.t. by 6·1°, 1 per cent. of *iso*butyl alcohol by 0·7°, and 1 per cent. of *sec.*-butyl alcohol by 1·9°. The relations of the c.s.t.'s of isomerides are being more fully examined.

The values of the c.s.t. in table V were obtained when the quantities of the two constituents delivered respectively by the two pipettes were used, that is, 1 c.c. of the standard hydrochloric acid and 0·4958 c.c. of impure *n*-butyl alcohol. The "percentage" of admixture is by weight in the *n*-butyl alcohol.

TABLE V.

Water present, per cent.	0	2·677	2·796	10·75	4·034
Upper c.s.t.	43·55°	45·7°	46·2°	52·35°	47·95°
Lower c.s.t.	9·6	8·2	7·9	3·0	6·5
Toluene present, per cent.	0	0·1422	0·3157	0·5077	
Upper c.s.t.	43·55°	47·4°	50·1°	53·2°	
Lower c.s.t.	9·6	5·8	3·15	−1·15	
Amyl alcohol present, per cent.	0	0·5910	0·8366	2·666	1·415
Upper c.s.t.	43·55°	46·95°	47·6°	53·8°	50·1°
Lower c.s.t.	9·6	6·75	5·8	−0·9	3·25
Ethyl alcohol present, per cent.	0	0·6288	0·2381		
Upper c.s.t.	43·55°	35·3°	40·1°		
Lower c.s.t.	9·6	16·8	12·8		

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CX.—*The Action of Grignard Reagents on the Esters of Certain Dicarboxylic Acids.*

By HARRY HEPWORTH.

THE action of Grignard reagents on the esters of the simpler saturated aliphatic dicarboxylic acids has been the subject of several investigations. Valeur (*Compt. rend.*, 1901, **132**, 833) obtained ditertiary glycols by the action of magnesium methyl iodide and magnesium ethyl iodide on ethyl oxalate, ethyl malonate, and ethyl succinate, and somewhat later (*Compt. rend.*, 1903, **136**, 694) prepared benzopinacone and tetraphenylbutanediol by the

action of magnesium phenyl bromide on methyl oxalate and ethyl succinate respectively. Dilthey and Last (*Ber.*, 1904, **37**, 2639) claimed to have prepared β-benzopinacolin from ethyl oxalate, and magnesium phenyl bromide, and diphenylphenacylcarbinol, $COPh{\cdot}CH_2{\cdot}CPh_2{\cdot}OH$, from ethyl succinate in a similar way. Valeur, however, still claimed that the product of the action of magnesium phenyl bromide on methyl or ethyl oxalate is benzopinacone (*Compt. rend.*, 1904, **139**, 480). Again, Harries (*Annalen*, 1905, **343**, 363) prepared βε-dimethylhexane-βε-diol, $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$, by the interaction of magnesium methyl iodide and ethyl succinate. In all these investigations the experimental conditions have been such as would favour attack on both carboxyalkyl groups by the Grignard compound employed, with the result that almost invariably fully substituted glycols or compounds of an analogous nature have been produced.

An exception arises in the work of Slavjanov (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 140), who, during the course of some experiments on the preparation of hexamethyl*cyclo*propane, incidentally obtained some β-hydroxy-ααβ-trimethylbutyric acid,

$$OH{\cdot}CMe_2{\cdot}CMe_2{\cdot}CO_2H,$$

by the action of magnesium methyl iodide on methyl dimethylmalonate. The only other evidence of selective action of Grignard reagents on one of the two carboxyalkyl groups of the esters of the simpler aliphatic dicarboxylic acids appears to be that of Egorova (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1454), who acted on ethyl oxalate with magnesium *tert.*-butyl chloride, and obtained, amongst other products, α-hydroxy-ββ-dimethylbutyric acid, $CMe_3{\cdot}CH(OH){\cdot}CO_2H$, and α-ethoxy-ββ-dimethylbutyric acid, $CMe_3{\cdot}CH(OEt){\cdot}CO_2H$; whilst, in the hope of finding a convenient method of obtaining α-ketonic acids, the action of Grignard reagents on ethyl oxalate was investigated by Inglis and Mason (P., 1909, **25**, 195), but the work described in this note is incomplete and does not appear to have been subsequently published.

In view of the fact that the discrepancy between the observations of Slavjanov (*loc. cit.*) and the results of other workers might be attributed either to a form of steric hindrance exerted by the methyl-substituting groups of the ester of dimethylmalonic acid or to the fact that Slavjanov used only three equivalents of magnesium and methyl iodide, whereas Valeur, Dilthey, and Harries used at least four equivalents, it was decided to carry out experiments to ascertain whether, by suitable control, the action of the Grignard reagent on the esters of certain aliphatic dicarboxylic acids could be confined to one carboxyalkyl group.

In this connection, it is interesting to note that Grignard

reagents react in a rather anomalous and unexpected manner with ethyl acetoacetate and its alkyl derivatives. Thus Grignard has shown (*Compt. rend.*, 1902, **134**, 849) that magnesium methyl iodide and ethyl acetoacetate give methane, hydrogen, and unchanged ester, the ester thus reacting in the enolic form. On the other hand, the monoethyl derivative of ethyl acetoacetate and magnesium methyl iodide react to give some ethyl β-hydroxy-α-ethyl*iso*valerate, $OH{\cdot}CMe_2{\cdot}CHEt{\cdot}CO_2Et$, whilst methyl diethylacetoacetate does not react at all. Again, McKenzie (T., 1906, **89**, 380) has shown that menthyl acetoacetate reacts as though entirely enolic.

Experiments have been carried out on the action of magnesium methyl iodide and magnesium ethyl bromide on ethyl oxalate, ethyl malonate, ethyl ethylmalonate, ethyl dimethylmalonate, and ethyl succinate, using about 2·5 equivalents of magnesium and alkyl haloids to one of ester. With the exception of ethyl malonate, which appears to react entirely in the enolic form, the reaction has been so regulated as to confine the action of the Grignard compound almost completely to one carboxyalkyl group.

In these experiments it was not found necessary to prepare the Grignard reagent separately, as the best results were obtained by dropping a mixture of alkyl haloid and ester into a well-stirred and cooled mixture of magnesium powder and dry ether (compare Davies and Kipping, T., 1911, **99**, 296). The mixture of alkyl haloid and ester was added at such a rate as to keep the reaction just perceptibly in progress.

In this way α-hydroxy*iso*butyric acid and α-hydroxy-α-ethylbutyric acid were prepared from ethyl oxalate, β-hydroxy-α-ethyl*iso*valeric acid from ethyl ethylmalonate, β-hydroxy-αα β-trimethylbutyric acid from ethyl dimethylmalonate, and *iso*hexolactone and γ-ethyl-*n*-hexolactone from ethyl succinate.

Now Shibata has shown (T., 1909, **95**, 1449) that Grignard reagents react with ortho-phthalic esters to give derivatives of phthalide, in which only one carboxyalkyl group of the phthalic ester is attacked. He compares this reaction with the production of tetra-alkylbutanediols from ethyl succinate and Grignard compounds (Valeur, *loc. cit.*), and concludes from this, together with the work of Bethmann (*Zeitsch. physikal. Chem.*, 1890, **5**, 409) on succinic acid, that in the latter compounds the two carboxyl groups are in the *trans*-position, whereas in *o*-phthalic acid the carboxyl groups are in the *cis*-position. It has now been shown that the action of the Grignard compound may be confined to one carboxyalkyl group in the case of ethyl succinate with the production of γγ-dialkylbutyrolactones, from which it might equally well be

concluded that the two carboxyl groups in succinic acid are in the *cis*-position. All that can be safely inferred, however, seems to be that in the intermediate compounds obtained by the interaction of Grignard compounds and ethyl succinate or orthophthalic esters, the hydroxyl and carboxyalkyl groups are possibly in the *cis*-position, and in the absence of any strictly quantitative data it is somewhat hazardous to draw any conclusions as to the steric structures of succinic and phthalic acids from such observations.

Experimental.

Preparation of α-Hydroxy-α-ethylbutyric Acid from Ethyl Oxalate.

Three hundred grams of dry ether and 10 grams of magnesium powder were introduced into a wide-necked flask provided with a stirrer, dropping funnel, and condenser, and surrounded by ice. Ten grams of ethyl bromide were placed in the flask, and after the reaction had started a mixture of 73 grams of ethyl oxalate and 126 grams (2·5 mols.) of ethyl bromide was added at such a rate as to keep the reaction proceeding slowly. The rest of the magnesium, 21 grams (2·5 mols.), was added from time to time so as to keep the magnesium always in excess. Towards the end of the reaction the contents of the flask became very viscous. Stirring was continued for an hour after the whole of the magnesium had been added, after which the mixture was allowed to remain overnight at the ordinary temperature.

The mixture was then heated on a water-bath for two hours and, after cooling, ice-cold water followed by 40 per cent. sulphuric acid was slowly added until the whole of the magnesium had dissolved.

A brown oil separated, and after its removal the residue was extracted four times with ether. The oil and ethereal extract were combined, dried over anhydrous sodium sulphate, and the ether removed by distillation, when 61 grams of a brown, rather viscous oil remained.

This oil was then distilled, when about 53 grams passed over between 172° and 185°. At 210° there was evidence of decomposition and the distillation was stopped. The fraction distilling at 172—185° was fractionated in a five-pear column, when about 48 grams distilled at 174—180° and about 4 grams at 180—186°. The latter proved to be principally unchanged ethyl oxalate.

The fraction distilling at 174—180° was redistilled, when 45·5 grams (57 per cent.) of ethyl α-hydroxy-α-ethylbutyrate distilled at 175—177° (corr.) (Frankland and Duppa, *Annalen*, 1863, **126**, 109).

Sixteen grams of the ester were boiled under reflux with 5 grams

(1¼ mols.) of sodium hydroxide for two hours. After cooling and acidifying, a solid separated, which was removed, and the residue extracted six times with ether. There were obtained 12 grams of an acid, which crystallised from light petroleum in long needles melting at 79·5°.

The identity of this acid with α-hydroxy-α-ethylbutyric acid was established by conversion into its barium salt (Found, Ba = 34·22; calc., Ba = 34·3 per cent.) and by its conversion into the ethyl*iso*crotonic acids on repeated distillation (Fittig, *Annalen*, 1904, **334**, 101).

*Preparation of α-Hydroxy*isobutyric *Acid from Ethyl Oxalate.*

This was carried out on exactly the same lines as the preparation of α-hydroxy-α-ethylbutyric acid described above, except that methyl iodide was used instead of ethyl bromide. Seventy-three grams of ethyl oxalate were treated with 30 grams (2·5 mols.) of magnesium powder and 180 grams (2·5 mols.) of methyl iodide; 39·6 grams (60 per cent.) of an oil boiling at 150—151° were obtained, and the identity of this with ethyl α-hydroxy*iso*butyrate was confirmed by conversion of 10 grams of the ester into the acid. The latter melted at 78° and the barium salt was analysed (Found, Ba = 39·82; calc., Ba = 39·98 per cent.) (Frankland and Duppa, *Annalen*, 1865, **133**, 80; Fittig, *ibid.*, 1877, **188**, 54).

Several attempts were made to increase these yields by variations in the addition of the reagents, but in no case was a yield greater than 60 per cent. obtained. Unless the addition of alkyl haloid and ester is made very slowly, a considerable amount of a by-product, which is probably a butanediol, is formed.

*Preparation of γ-Ethyl-*n*-hexolactone from Ethyl Succinate.*

Eighty-seven grams of diethyl succinate (b. p. 215—216°) were treated with 30 grams (2·5 mols.) of magnesium powder and 136 grams (2·5 mols.) of ethyl bromide in 400 c.c. of dry ether as described in the preparation of ethyl α-hydroxy-α-ethylbutyrate. After removal of the ether, an oil was obtained, of which the greater part distilled at 125—140°/23 mm., although a little passed over at 120—123°. The former fraction, weighing 32 grams, was fractionated under the ordinary pressure, when 26 grams distilled at 227—232° (corr.). This fraction was freed from any unchanged ethyl succinate by boiling under reflux with 15 grams of sodium hydroxide for two hours, acidifying with concentrated hydrochloric acid, and boiling for a further half-hour, when an oil separated

on the surface. This was removed and the residue extracted eight times with ether. The oil and ethereal extract were then combined and washed with a little sodium carbonate to remove succinic acid. After removal of the ether, 27 grams of an oil remained, which on redistillation boiled at 229—231° (corr.).

A further 6 grams of the lactone were obtained by working up the fraction distilling at 120—123°/23 mm. The total yield was 33 grams (46 per cent. of the theoretical).

The identity of this compound with γ-ethyl-*n*-hexolactone was established by its conversion into the barium salt of γ-hydroxy-γ-ethyl-*n*-hexoic acid (Wischen, *Annalen*, 1867, **143**, 262; Emmert, *Ber.*, 1888, **15**, 1851). The latter was obtained as an amorphous powder, readily soluble in water or alcohol, which on recrystallisation from alcohol gave Ba = 30·12 (calc., Ba = 30·17 per cent.).

Preparation of iso*Hexolactone from Ethyl Succinate.*

Eighty-seven grams of diethyl succinate were treated with 30 grams (2·5 mols.) of magnesium and 177 grams (2·5 mols.) of methyl iodide exactly as described above. An oil (57 grams: 50 per cent. of the theoretical) was eventually obtained which boiled at 200—202° (Blanc, *Compt. rend.*, 1904, **138**, 579; **139**, 65). The identity of this with *iso*hexolactone was established by conversion into the barium salt of γ-hydroxy*iso*hexoic acid (Found, Ba = 34·3; calc., Ba = 34·3 per cent.).

Experiments were carried out in which the whole of the ethyl succinate was placed in the flask and the ethyl bromide slowly added, but the reaction was more difficult to control and no greater yield was obtained.

Action of Magnesium Methyl Iodide on Ethyl Malonate.

A mixture of 16 grams of ethyl malonate (b. p. 198°) and 36 grams of methyl iodide (2·5 mols.) was added drop by drop to 6 grams of magnesium in 100 c.c. of dry ether as described under the preparation of α-hydroxy-α-ethylbutyric acid from ethyl oxalate. On decomposing the product with water and dilute sulphuric acid, the greater part of the ethyl malonate was recovered unchanged. From this it would appear that under these conditions ethyl malonate reacts in the enolic form.

Action of Magnesium Methyl Iodide on Ethyl Ethylmalonate.

A mixture of 19 grams of ethyl ethylmalonate (b. p. 204—206°) and 36 grams of methyl iodide (2·5 mols.) was added drop by drop

to a well-cooled and stirred mixture of 6 grams of magnesium and 100 c.c. of dry ether as described before. The mixture was allowed to remain overnight at the ordinary temperature and then heated under reflux, on a water-bath, for three hours.

After decomposing, an oil was obtained, the greater part of which distilled at 200—207° and proved to be ethyl ethylmalonate. About 5 grams of a fraction of higher boiling point (220—240°) was collected, and on hydrolysis gave an acid which, when crystallised from light petroleum containing a little acetone, melted at 72°. This acid appeared to be β-hydroxy-α-ethyl*iso*valeric acid, obtained by Grignard (*Compt. rend.*, 1902, **134**, 849) by the action of magnesium methyl iodide on ethyl ethylacetoacetate. The barium salt on analysis gave Ba = 32·07 (calc., Ba = 32·11 per cent.)

Action of Magnesium Methyl Iodide on Ethyl Dimethylmalonate.

Slavjanov (*loc. cit.*) obtained ββδ-dihydroxy-βγγδ-tetramethylpentane and β-hydroxy-ααβ-trimethylbutyric acid by heating one equivalent of ethyl dimethylmalonate with three equivalents of magnesium and methyl iodide in the presence of dry ether, on a water-bath for three to five hours.

A mixture of 19 grams of ethyl dimethylmalonate and 36 grams of methyl iodide (2·5 mols.) was added drop by drop to a well-cooled and stirred mixture of 6 grams of magnesium in 100 c.c. of dry ether, as decribed before. The mixture was allowed to remain overnight at the ordinary temperature, and then heated under reflux on a water-bath for three hours.

After decomposing, an oil separated which on distillation gave a fraction (9 grams) boiling at 190—210° and a second fraction (7 grams) boiling at 220—250°. The former proved to be ethyl dimethylmalonate, whilst the latter, on hydrolysis, gave an acid which on purifying by sublimation melted at 151—152°. This acid appeared to be identical with β-hydroxy-ααβ-trimethylbutyric acid first prepared by Reformatsky (*Ber.*, 1895, **28**, 2839). During the hydrolysis of the fraction boiling at 220—250° a little insoluble material remained, which on recrystallisation melted at 77°. This was probably ββδ-dihydroxy-βγγδ-tetramethylpentane, but there was insufficient material for further examination.

Preliminary experiments on this investigation were carried out at University College, Nottingham, in 1915, under the direction of Prof. Kipping.

The author is indebted to the Research Committee of Messrs.

Nobel's Explosives Co., Ltd., and particularly to Mr. Rintoul, for the facilities accorded him for the completion of this work, and also to Mr. Carr, of Messrs. Boots, Ltd., for permission to publish certain portions of this investigation.

THE RESEARCH LABORATORIES,
ARDEER.

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CXI.—*The Melting Points of the Substituted Amides of the Normal Fatty Acids.*

By PHILIP WILFRED ROBERTSON.

OUR knowledge of the physical properties of homologous series is largely due to the researches of Krafft. Whereas the densities approximate to a constant value as the series is ascended, the melting points and boiling points continue to rise, although the successive differences become smaller and smaller. To this general rule, however, the normal fatty acids form a noteworthy exception, since their melting points fall to a minimum and then subsequently rise, and further since the values for the odd and the even members fall on two distinct curves. This exceptional behaviour has been attributed to the association of the earlier members of the series, which itself is probably not unconnected with the arrangement of the atoms in space. Some years ago it was pointed out (Robertson, T., 1908, **93**, 1033) that the amides, anilides, and *p*-toluidides showed an even greater irregularity, which was explained, rather vaguely, as being due to molecular dissymmetry. In the hope of obtaining a nearer insight into the relationship between melting point and chemical composition, certain new series, in particular, bromo-derivatives, have now been investigated. In the meantime a systematic search through the earlier and more recent literature had revealed a considerable discrepancy between the values published by different observers; in some cases the melting points given for a compound differed by as much as 20°. In these circumstances it was felt necessary to make a complete redetermination of the melting points of these series. The correctness of a given melting point would appear to depend essentially on the following factors: (*a*) the identity of the normal fatty acid employed in the preparation, (*b*) its purity, and especially its freedom from neighbouring homologues, which in the final product can be separated often only with the greatest difficulty; (*c*) the purity of the product (especially when it is very readily soluble and tends to separate as an oil),

which was attained by numerous recrystallisations from different solvents; (*d*) the accuracy of the melting point determination. As is indicated in the sequel, every effort has been made to fulfil these conditions.

The melting points of the amides, anilides, *p*-toluidides, *o*-toluidides, *p*-bromoanilides, *o*-bromo-*p*-toluidides, tribromo-anilides, β-naphthylamides, and α-bromo-β-naphthylamides are collected in the following tables. Each series will first of all be considered separately and then the results will be discussed as a whole.

TABLE I.

No. of carbon atoms in chain.	Amides. M. p.	Anilides. M. p.	*p*-Toluidides. M. p.
2	82°	112°	153°
3	77°	106°	126°
4	115	96	75
5	106	63	74
6	101	92	73
7	96	65	80
8	105	55	70
9	99	57	84
10	99	70	78
11	99	71	80
12	100	78	87
13	100	80	88
14	103	84	93
15	—	—	—
16	106	89	98
17	—	—	—
18	109	94	102

Amides (Table I; Fig. 1).

As is clearly visible in the figure, the melting points of the odd and even members fall on two distinct curves, which, although not superposable, rise and fall in the same manner at corresponding places. The initial rise is characteristic only of the amides; the substituted amides, and the fatty acids also, show a fall in melting point at the beginning of the series. It is to be noted that the lower fatty amides, like the corresponding acids, are considerably associated; but the type of melting-point curve is quite different in the two series.

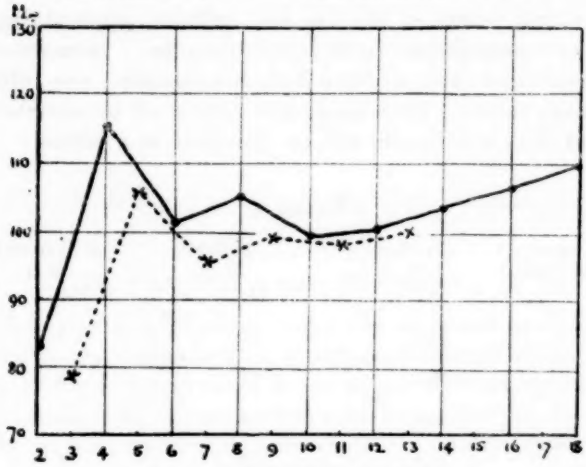
Anilides (Table I; Fig. 2).

The melting points of the even anilides fall to a sharp minimum at the eighth member, with a noticeable flattening between the fourth and sixth members. The large fall in melting point between the C_6 and the C_8 anilide, no less than 37°, is very remarkable.

FIG. 1.

Amides.

(Even members ——: odd members - - - - -)

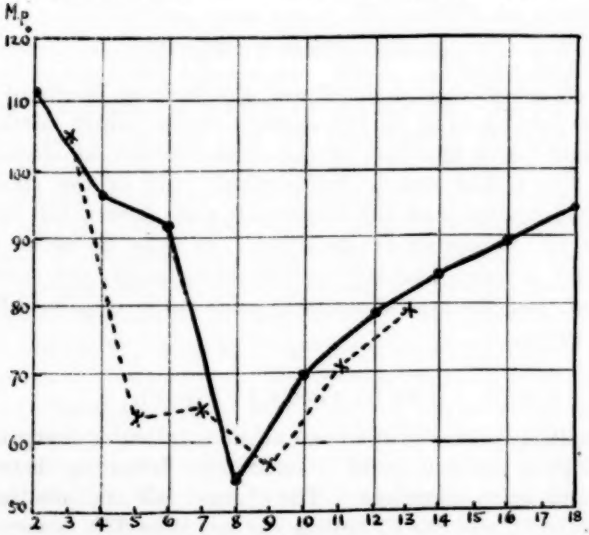


No. of carbon atoms in chain.

FIG. 2.

Anilides.

(Even members ——; odd members - - - - -)



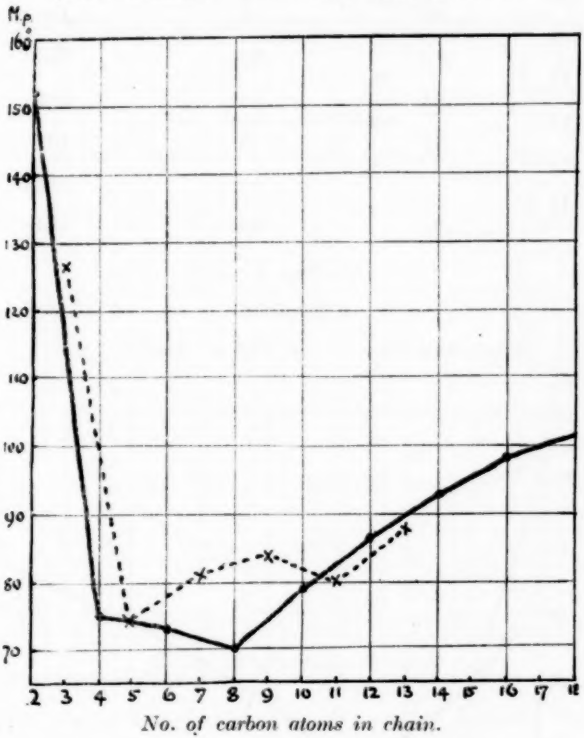
No. of carbon atoms in chain.

The odd series shows a similar large fall followed by a slight rise at the fifth member, corresponding with the flattening in the even series. It is to be noticed that this curve is, at the beginning, exactly the reverse of the odd curve of the amides. The factor causing the irregularity apparently is acting in the reverse sense in

FIG. 3.

p-Toluidides.

(Even members ——— ; odd members - - - - -



No. of carbon atoms in chain.

two series until its effect is eliminated by another factor, some function of the molecular weight, which begins to operate higher in the series.

p-Toluidides (Table I; Fig. 3).

The introduction of a methyl group in the para-position of the anilides causes a fundamental change in the melting-point relationships. In the even series the noticeably large initial fall is followed by a very slow decrease to the minimum at the eighth member.

In the odd series, on the other hand, the initial fall is followed by a slight rise and subsequent fall to a second minimum at the eleventh member.

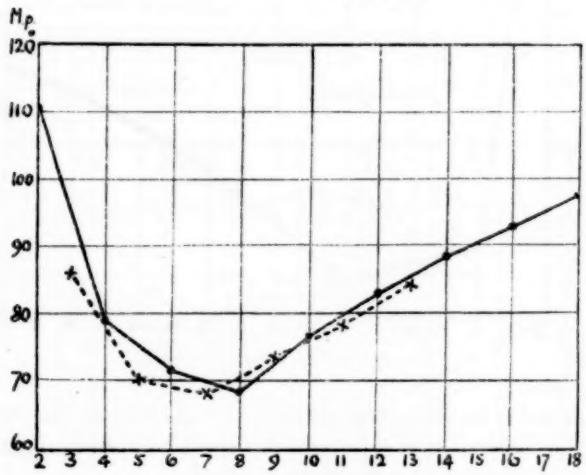
TABLE II.

No. of carbon atoms in chain.	*o*-Toluidides. M. p.	*o*-Bromo-*p*-toluidides. M. p.	*p*-Bromo-anilides. M. p.
2	110°	118°	167°
3	87°	111°	149°
4	79	90	115
5	70	100	108
6	71	84	105
7	68	90	98
8	69	78	103
9	73	86	100
10	76	82	102
11	78	91	102
12	83	85	104
13	85	95	—
14	88	89	107
15	—	—	—
16	—	—	110
17	—	—	—
18	97	97	114

FIG. 4.

o-Toluidides.

(Even members ——; odd members - - - - -)



o-Toluidides (Table II; Fig. 4).

Both the odd and even members form the typical curve, that is, the melting points fall to a minimum and then rise again with increasing slowness as the series is ascended.

In Figs. 1 to 4 it is seen that after the eleventh member the melting points of the odd compounds fall slightly below the even values, which behaviour characterises the fatty acids also. This appears to be the general rule, to which the next series is, however, an exception.

o-*Bromo*-p-*toluidides* (Table II; Fig. 5).

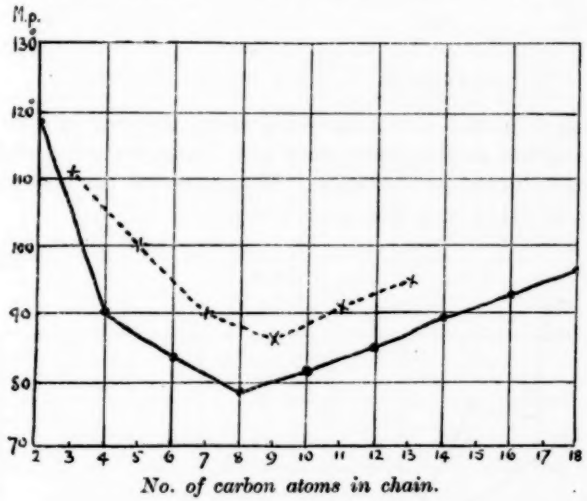
The even and the odd series form typical curves, approximately parallel to each other.

Whereas the odd melting points generally tend to coincide with or fall slightly below the even values, at all events with compounds

FIG. 5.

o-*Bromo*-p-*toluidides*.

(Even members ——; odd members - - - - -)



of high molecular weight, here their average melting point is no less than 6° higher. It has not been found possible to correlate this noticeable difference in behaviour with any other characteristic of the series.

p-*Bromo-anilides* (Table II; Fig. 7).

As is seen in Fig. 7, in which the melting points of the even series only are plotted, there is a large fall from the second to the fourth member, followed by a further slow fall to a minimum at the C_{10} compound. The odd values fall somewhat below the even and show a minimum at the seventh member.

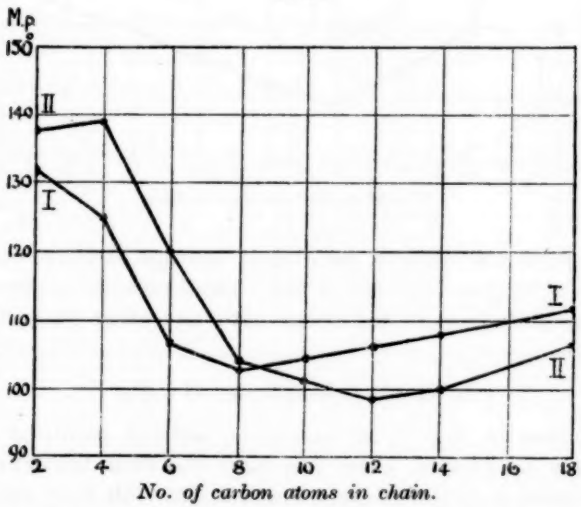
TABLE III.

No. of carbon atoms in chain.	2:4:6-Tribromo-anilides. M. p.	β-Naphthylamides. M. p.	α-Bromo-β-naphthylamides. M. p.
2	232°	132°	138°
3	203°	—	139°
4	179	125	139
5	—	112°	136
6	136	107	120
7	134	101	111
8	131	103	104
9	131	103	103
10	129	104	102
11	129	—	—
12	126	106	99
13	—	107	—
14	124	108	100
15	—	—	—
16	124	—	—
17	—	—	—
18	126	112	106

2:4:6-*Tribromo-anilides* (Table III; Fig. 7).

The rapid initial fall in melting point noticed in the *p*-bromo-anilides beomes in this series even more exaggerated, and the minimum is now higher in the series. The curve for the odd members is almost coincident with the even curve.

FIG. 6

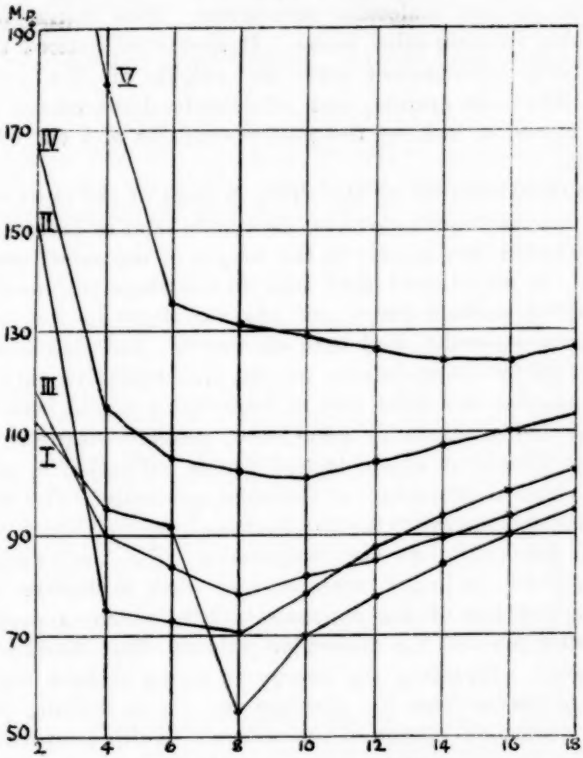


I. *β-Naphthylamides.* II. *α-Bromo-β-naphthylamides.*

β-Naphthylamides (Table III; Fig. 6).

The comparatively slow initial fall in melting point differentiates this series from those hitherto considered. The curve for the odd members at first falls slightly below and then coincides with the even curve.

FIG. 7.



No. of carbon atoms in chain.

I. *Anilides.* II. p-*Toluidides.* III. o-*Bromo*-p-*toluidides.* IV. p-*Bromo-anilides.* V. *Tribromo-anilides.*

α-Bromo-β-naphthylamides (Table III; Fig. 6).

The effect of introducing a bromine atom is to change the initial slow fall in melting point of the β-naphthylamides into a very slight rise, and to cause the minimum to occur higher in the series. The curves for the odd and even members tend to coincide.

General Discussion.

From an inspection of Fig. 7, in which several typical curves are collected, it appears that the higher melting-point curves (*a*) have a

greater initial fall, (*b*) are flatter in the neighbourhood of the minima, (*c*) have minima which occur higher up in the series.

If the initial fall in melting point is to be attributed to the greater association of the earlier members, as in the case of the fatty acids, it might be expected to become much less for a series of compounds like the tribromo-anilides, in which the diortho-grouping would prevent molecular association. This initial fall must then be due to some other cause. It should be noticed that it is at all events unconnected with the weight of the substituent radicle. Thus the anilides and *p*-toluidides have totally different types of curve, as likewise the *p*-bromo-anilides and the *o*-bromo-*p*-toluidides.

At a certain distance up the series, in most of the cases examined at about the fourteenth member, the curves tend to become parallel, rising somewhat less rapidly as the weight of the substituent group increases. It would seem then that at this stage the causes of the initial fall in melting point, and the variations in the early part of the curve generally, had been eliminated, and that some single factor, probably the molecular weight, was operative only.

The molecules of a solid may be regarded as being held together in a condition of strain by some force, possibly magnetic (Oxley), on the magnitude of which depend double refraction in particular and the physical properties of the solid generally. The energy of the molecules is almost entirely vibrational, half of which is kinetic and half potential. As the temperature rises the amplitude of vibration of the molecule increases, and when it becomes equal to the mean distance of the molecules apart, which is proportional to the cube root of the molecular volume, the substance melts (Lindemann). Equating the energy in terms of heat required to raise the molecule from the absolute zero to its melting point, T_s, with the vibrational energy of the molecule at this temperature, one obtains the expression

$$MsT_s = \kappa \cdot MV^{\frac{2}{3}}\nu^2 \quad (\kappa = \text{const.}),$$

where M is the molecular weight, s the mean specific heat from the absolute zero to T_s, V the molecular volume, and ν the characteristic vibration frequency of the molecule.

It is thus seen that the melting temperature is a function of the specific heat, the molecular volume, and the vibration frequency of the molecule. A suitable variation of these three values would be capable of causing the observed irregularities in the melting points of a series of compounds. This equation also shows that the magnitude of the melting point is independent of any association in the liquid phase, although it is probable that the factors causing

such association would effect the values of s, V, and v in the sense of increasing the value of T_s.

High up a series the density and specific heat of successive members become approximately constant, and then

$$T_s = \kappa' \cdot M^{\frac{1}{3}} v^2 \quad (\kappa' = \text{const.}).$$

Under such conditions v is probably some simple function of M, so that the melting point might be expected to depend on the magnitude of the molecular weight alone. Actually the empirical relation,

$$T_s = \kappa'' \cdot M^{\frac{1}{3}} \quad (\kappa'' = \text{const.}),$$

has been found, with two noticeable exceptions, to give a fair agreement, not only for the higher members of the substituted amides, but for other compounds also (table IV).

TABLE IV.

Compound.	Rise in m. p. for $2CH_2$. Experimental.*	From formula.
C_{16} anilide	5·0°	4·7°
C_{16} *p*-toluidide	4·5	4·6
C_{16} *o*-toluidide	4·5	4·6
C_{16} *p*-bromoanilide	4·0	4·0
C_{16} *o*-bromo-*p*-toluidide	4·0	3·9
C_{16} α-bromo-β-naphthylamide	3·0	3·2
C_{16} amide	3·0	6·1
C_{16} β-naphthylamide	2·0	4·3
Triacontane, $C_{30}H_{62}$	3·9	3·6
Montanone, $C_{55}H_{110}O$	1·8	2·2

* For the substituted amides, the mean difference between the C_{14} and C_{18} compounds was taken; in the other cases, a slight interpolation was necessary.

EXPERIMENTAL.

The substituted amides obtained in this investigation were prepared in the following manner. About 1 gram of the fatty acid was mixed in a test-tube with slightly more than the theoretical quantity of thionyl chloride and heated to 100—120° in a sulphuric acid bath for about an hour. The theoretical quantity of base was then added, and the mixture further heated for half an hour to a somewhat higher temperature. The product was recrystallised from alcohol until the melting point was constant, and then finally from light petroleum, with which was mixed, in the case of the less soluble compounds, a small quantity of benzene.

The fatty acids employed were obtained from Kahlbaum. The purity of the solid acids was tested by determining their melting points; the liquid acids were either synthetic or were compared

with Merck's preparations by preparing a common derivative and testing by the method of mixed melting point. The bases were purified by several recrystallisations before being used for the preparations.

Repeated attempts were made to discover the existence of physical isomerides by recrystallising the same compound from different solvents and at different temperatures, and also by having present a trace of alkali or of acid in the solution. All these experiments, however, were without result.

All the melting-point determinations were made by the capillary tube method in a castor-oil bath with the same thermometer, which was compared from time to time with a standard one. When it happened that neighbouring members of a series melted at about the same temperature, their melting points were redetermined simultaneously.

The amides not containing bromine were analysed by the methods of Dumas or Kjeldahl. The bromo-derivatives were analysed by the chromic acid method,* which with practice enables an estimation to be made in about fifty minutes.

In table V are given the redetermined values of the melting points of the amides, anilides, and *p*-toluidides. The values given by other observers are included for the sake of comparison.

TABLE V.

Compound.	Formula.	M. p.	Previous observers.
n-Valeramide	$C_5H_{11}ON$	106°	115° (Weidel); 105° (Fournier); 102° (Hofmann).
n-Hexoamide	$C_6H_{13}ON$	101	100° (Hofmann).
n-Heptoamide	$C_7H_{15}ON$	96	96° (Hofmann); 95° (Mehlis); 95° (Fournier); 95° (Malherba); 94° (Aschan).
n-Octoamide	$C_8H_{17}ON$	105	110° (Felletar); 106° (Hofmann); 98° (Aschan).
n-Nonoamide	$C_9H_{19}ON$	99	99° (Hofmann); 93° (Schalfejew).
n-Decoamide	$C_{10}H_{21}ON$	99	108° (Ehestadt); 98° (Hofmann).
n-Undecoamide	$C_{11}H_{23}ON$	99	103° (Ehestadt); 81° (Lwow).
Lauramide	$C_{12}H_{25}ON$	100	110° (Ehestadt); 102° (Krafft); 99° (Caspari); 97° (Lutz).
n-Tridecoamide	$C_{13}H_{27}ON$	100	98° (Lutz).
Myristamide	$C_{14}H_{29}ON$	103	102° (Reimer).
Palmitamide	$C_{16}H_{33}ON$	106	107° (Krafft); 105° (Hell); 101° (Carlet).
Stearamide	$C_{18}H_{37}ON$	109	109° (Krafft); 108° (Hell); 107° (Carlet).
n-Butyranilide	$C_{10}H_{13}ON$	96	97° (Beneck); 93° (Fournier); 92° (Kelbe); 90° (Gerhardt); 90 (Autenrieth).

* Robertson, T., 1915, **107**, 902. The following slight modifications have been introduced. Sodium peroxide is used instead of perhydrol, and *N*/20-silver nitrate and thiocyanate in place of *N*/10-solutions.

TABLE V (*continued*).

Compound.	Formula.	M. p.	Previous observers.
n-Valeranilide	$C_{11}H_{15}ON$	63°	63° (Fournier); 61° (Easterfield); 60° (Majima).
n-Hexoanilide	$C_{12}H_{17}ON$	92	95° (Kelbe).
n-Heptoanilide	$C_{13}H_{19}ON$	65	71° (Lwow).
n-Octoanilide	$C_{14}H_{21}ON$	55	57° (Robertson).
n-Nonoanilide	$C_{15}H_{23}ON$	57	57° (Robertson).
n-Decoanilide	$C_{16}H_{25}ON$	70	61° (Robertson).
n-Undecoanilide	$C_{17}H_{27}ON$	71	68° (Bagard); 64° (Robertson).
Lauranilide	$C_{18}H_{29}ON$	78	76° (Caspari); 68° (Robertson).
n-Butyro-*p*-toluidide	$C_{11}H_{15}ON$	75	74° (Robertson).
n-Valero- ,,	$C_{12}H_{17}ON$	74	72° (Robertson).
n-Hexo- ,,	$C_{13}H_{19}ON$	73	75° (Robertson).
n-Hepto- ,,	$C_{14}H_{21}ON$	81	80° (Robertson); 79° (Kipping).
n-Octo- ,,	$C_{15}H_{23}ON$	70	67° (Robertson).
n-Nono- ,,	$C_{16}H_{25}ON$	84	81° (Robertson).
n-Deco- ,,	$C_{17}H_{27}ON$	78	80° (Robertson).
n-Undeco- ,,	$C_{18}H_{29}ON$	80	75° (Bagard); 73° (Robertson).
Lauro- ,,	$C_{19}H_{31}ON$	87	81° (Robertson).
Myristo- ,,	$C_{21}H_{35}ON$	93	93° (Robertson).
Palmito- ,,	$C_{23}H_{39}ON$	98	96° (Robertson).
Stearo- ,,	$C_{27}H_{43}ON$	102	98° (Robertson).

In table VI are given the new compounds prepared in this investigation, with melting points and analytical results; the percentage values refer to bromine in the case of the bromo-derivatives and to nitrogen for the other compounds.

TABLE VI.

Compound.	Formula.	M. p.	Found per cent.	Calc. per cent.
n-Tridecoanilide	$C_{19}H_{31}ON$	80°	N=4·7	4·8
n-Trideco-*p*-toluidide	$C_{20}H_{33}ON$	88	4·4	4·6
n-Butyro-*o*-toluidide	$C_{11}H_{15}ON$	79	8·0	7·8
n-Hexo- ,,	$C_{13}H_{19}ON$	71	6·6	6·8
n-Hepto- ,,	$C_{14}H_{21}ON$	68	6·5	6·4
n-Octo- ,,	$C_{15}H_{23}ON$	69	6·2	6·0
n-Nono- ,,	$C_{16}H_{25}ON$	73	5·4	5·7
n-Deco- ,,	$C_{17}H_{27}ON$	76	5·2	5·3
n-Undeco- ,,	$C_{18}H_{29}ON$	78	5·0	5·0
Lauro- ,,	$C_{19}H_{31}ON$	83	4·9	4·8
n-Trideco- ,,	$C_{20}H_{33}ON$	85	4·8	4·6
Myristo- ,,	$C_{21}H_{35}ON$	88	4·5	4·4
Stearo- ,,	$C_{25}H_{43}ON$	97	3·8	3·8
n-Butyro-β-naphthylamide	$C_{14}H_{15}ON$	125	6·8	6·6
n-Valero- ,,	$C_{15}H_{17}ON$	112	6·2	6·2
n-Hexo- ,,	$C_{16}H_{19}ON$	107	5·6	5·8
n-Hepto- ,,	$C_{17}H_{21}ON$	101	5·7	5·5
n-Octo- ,,	$C_{18}H_{23}ON$	103	5·3	5·2
n-Nono- ,,	$C_{19}H_{25}ON$	103	5·1	4·9
n-Deco- ,,	$C_{20}H_{27}ON$	104	4·8	4·7
Lauro- ,,	$C_{22}H_{31}ON$	106	4·4	4·4
n-Trideco- ,,	$C_{23}H_{33}ON$	107	4·1	4·2
Myristo- ,,	$C_{24}H_{35}ON$	108	4·1	4·0
Stearo- ,,	$C_{28}H_{43}ON$	112	3·3	3·4

TABLE VI (*continued*).

Compound.	Formula.	M. p.	Found per cent.	Calc. per cent.
n-Butyro-*p*-bromoanilide.....	$C_{10}H_{12}ONBr$	115°	Br=33·4	33·1
n-Valero- ,, ...	$C_{11}H_{14}ONBr$	108	31·3	31·3
n-Hexo- ,, ...	$C_{12}H_{16}ONBr$	105	30·0	29·6
n-Hepto- ,, ...	$C_{13}H_{18}ONBr$	98	28·0	28·1
n-Octo- ,, ...	$C_{14}H_{20}ONBr$	103	26·8	26·9
n-Nono- ,, ...	$C_{15}H_{22}ONBr$	100	26·0	25·7
n-Deco- ,, ...	$C_{16}H_{24}ONBr$	102	24·6	24·6
n-Undeco- ,, ...	$C_{17}H_{26}ONBr$	102	23·7	23·7
Lauro- ,, ...	$C_{18}H_{28}ONBr$	104	22·3	22·6
Myristo- ,, ...	$C_{20}H_{32}ONBr$	107	20·8	20·9
Palmito- ,, ...	$C_{22}H_{36}ONBr$	110	19·8	19·5
Stearo- ,, ...	$C_{24}H_{40}ONBr$	114	18·4	18·3
Propio-*o*-bromo-*p*-toluidide	$C_{10}H_{12}ONBr$	111	33·4	33·1
n-Butyro- ,, ...	$C_{11}H_{14}ONBr$	90	30·9	31·3
n-Valero- ,, ...	$C_{12}H_{16}ONBr$	100	29·5	29·6
n-Hexo- ,, ...	$C_{13}H_{18}ONBr$	84	28·5	28·1
n-Hepto- ,, ...	$C_{14}H_{20}ONBr$	90	26·8	26·9
n-Octo- ,, ...	$C_{15}H_{22}ONBr$	78	25·5	25·7
n-Nono- ,, ...	$C_{16}H_{24}ONBr$	86	24·7	24·6
n-Deco- ,, ...	$C_{17}H_{26}ONBr$	82	23·7	23·7
n-Undeco- ,, ...	$C_{18}H_{28}ONBr$	91	22·3	22·6
Lauro- ,, ...	$C_{19}H_{30}ONBr$	85	21·3	21·7
n-Trideco- ,, ...	$C_{20}H_{32}ONBr$	95	21·0	20·9
Myristo- ,, ...	$C_{21}H_{34}ONBr$	89	20·6	20·3
Stearo- ,, ...	$C_{25}H_{42}ONBr$	97	17·7	17·7
Propio-α-bromo-β-naphthylamide	$C_{13}H_{12}ONBr$	139	29·0	28·8
n-Butyro- ,,	$C_{14}H_{14}ONBr$	139	27·3	27·4
n-Valero- ,,	$C_{15}H_{16}ONBr$	136	25·9	26·2
n-Hexo- ,,	$C_{16}H_{18}ONBr$	120	25·4	25·1
n-Hepto- ,,	$C_{17}H_{20}ONBr$	111	23·9	24·0
n-Octo- ,,	$C_{18}H_{22}ONBr$	104	23·4	23·1
n-Nono- ,,	$C_{19}H_{24}ONBr$	103	22·1	22·1
n-Deco- ,,	$C_{20}H_{26}ONBr$	102	21·7	21·3
Lauro- ,,	$C_{22}H_{30}ONBr$	99	19·5	19·8
Myristo- ,,	$C_{24}H_{34}ONBr$	100	18·6	18·5
Stearo- ,,	$C_{26}H_{42}ONBr$	106	16·4	16·4
n-Butyro-2:4:6-tribromoanilide	$C_{10}H_{10}ONBr_3$	179	58·8	58·3
n-Hexo ,,	$C_{12}H_{14}ONBr_3$	136	56·3	56·2
n-Hepto- ,,	$C_{13}H_{16}ONBr_3$	134	54·9	54·4
n-Octo- ,,	$C_{14}H_{18}ONBr_3$	131	52·8	52·6
n-Nono- ,,	$C_{15}H_{20}ONBr_3$	131	51·3	51·2
n-Deco- ,,	$C_{16}H_{22}ONBr_3$	129	49·9	49·7
n-Undeco- ,,	$C_{17}H_{24}ONBr_3$	129	48·0	48·2
Lauro- ,,	$C_{18}H_{26}ONBr_3$	126	46·8	46·9
Myristo- ,,	$C_{20}H_{30}ONBr_3$	124	44·0	44·5
Palmito- ,,	$C_{22}H_{34}ONBr_3$	124	42·1	42·3
Stearo- ,,	$C_{24}H_{38}ONBr_3$	126	40·6	40·3

The problem of investigating the relationship between melting point and chemical composition is being extended in other directions to the substituted amides of dibasic and α-substituted acids. The mathematical interpretation suggested above is from the nature

of things only fragmentary and imperfect, and it has not been possible to suggest a reason why compounds containing the grouping CO·NH· or CO·O· should form series so different in character from other series. The Quantum Theory has not yet been extended to include the investigation of complex molecules, but there is no doubt that a knowledge of the vibration frequency (ν), and the specific heat over a wide range of temperature, is essential for a complete mathematical treatment. The determination of the melting points of a large group of similar compounds is at all events a step in this direction.

My thanks are due to Dr. P. A. Levene for a specimen of tridecoic acid, and to the Chemical Society for a grant, which has partly defrayed the cost of the investigation.

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South Kensington.

[*Received, September 11th*, 1919.]

CXII.—*The Effect of Sea-salt on the Pressure of Carbon Dioxide and Alkalinity of Natural Waters.*

By Edmund Brydges Rudhall Prideaux.

The total "uncompensated base" or alkali present as carbonate and hydrogen carbonate in sea-water has been determined by Schlœsing and Dittmar and by many later investigators. The method used is nearly always titration with standard acid and an indicator of the methyl-orange class, and is subject to the errors of such titrations. The results, expressed in milli-equivalents per litre, are 2·48 (Schlœsing) and 2·41 (Dittmar). Moore, Herdman, and the author found values ranging from 2·36 to 2·50 (extreme values), average 2·44, in the water of the Irish sea from November, 1912, to July, 1913 (Herdman, "Report on the Lancashire Sea-Fisheries Scientific Investigations for 1914," *Trans. Biol. Soc. Liverpool*, 1915, **29**).

Fox (*Trans. Faraday Soc.*, 1909, **5**, 68), by boiling with excess of standard hydrochloric acid and titrating with standard sodium hydroxide and phenolphthalein, found the equivalent of 40 milligrams of hydroxylion on the average, or 2·35 milli-equivalents. The author, in June, 1913, using the same method, found 2·30.

The total carbonic acid may be obtained by boiling with an excess of sulphuric acid in a current of air and absorbing the carbon dioxide in standard barium hydroxide solution. In nearly all cases, however, the alkali of the carbonate and hydrogen carbonate, and hence the total carbon dioxide, has been obtained from the titrations with phenolphthalein and methyl-orange, the difference between these (in equivalents) being numerically equal to the number of molecules of carbonic acid present. The amount of water taken in the work referred to above is 100 c.c., to which five drops of 0·1 per cent. phenolphthalein are added, and the acid ($N/100$- or $N/50$-hydrochloric acid) is run in until the colour completely disappears. Then five drops of 0·1 per cent. dimethyl-aminoazobenzene or methyl-orange are added, and the titration is continued to a decided reddish-orange. With regard to the phenolphthalein titration, it may be remarked that in fresh water $N/10$- down to $N/1000$-hydrogen carbonate solutions are still slightly alkaline to phenolphthalein ($p_H = 8{\cdot}4$ to $8{\cdot}2$), and the titration should therefore be continued until a weak colour remains. In the case of sea-water, however, the p_H by extrapolation of the values given later and by direct measurement (see below) is 7·6. This, owing to the presence of salt, will appear to have a p_H of about 7·8. Consequently, the titration should be continued until the solution is quite colourless. The methyl-orange titrations in dilute solutions, and especially in such as contain salt, are likely to be high. This was verified in the standard carbonate solutions and neutral sea-water, and it was found that from 1 to 2 c.c. of $N/100$-hydrochloric acid should be subtracted from the titrations of 100 c.c. Thus the total alkali is probably 2·24 to 2·34 milli-equivalents per litre. Since the number of c.c. of $N/100$-acid required in the phenolphthalein titration is from 1 to 3 for 100 c.c. of water, that is, 0·1 to 0·3 milli-equivalents per litre, the value of R = equivalents of alkali ÷ molecules of carbonic acid is from $2{\cdot}3/2{\cdot}2 = 1{\cdot}04$ to $2{\cdot}3/2{\cdot}0 = 1{\cdot}15$. It may be noted that Schlœsing found carbonic acid equivalent to 98·3 milligrams of carbon dioxide and alkali equivalent to 99·3 milligrams of SO_3, from which $R = 1{\cdot}12$.

The alkalinities corresponding with all stages of neutralisation of carbonic acid at different concentrations have already been expressed as general equations (*Proc. Roy. Soc.*, 1915, [*A*], **91**, 535), and those which refer to the dilute solutions contain only the dissociation constants of carbonic acid and the water constant, together with the experimental quantities C = total concentration of carbonic acid and R the ratio of alkali to acid. From the curve (*loc. cit.*) connecting p_H and R, which agrees well with the

experimental alkalinities of hard water, etc., the following values have been taken in the row of calculated values:

C.	$R=$	1·06	1·08	1·10	1·12
0·001	$p_H=$	9·0	9·15	9·25	9·35 (calculated)
0·002	$p_H=$	8·7	8·9	8·95	8·9 (observed)

Obviously, the alkalinities are much greater than those found in the case of the same carbonate solutions present in sea-water. It seemed desirable to check experimentally this part of the curve in the case of fresh water.

Standard carbonate solutions were prepared by methods independent of indicators and titrations. Some $M/10$-sodium carbonate was made in the usual way. The factor, from the weight of sodium carbonate, was 1·015, by conversion into sodium sulphate 1·016, and by titration, using methyl-orange, 1·018. Some $N/10$-hydrochloric acid made by dilution from a known standard and again analysed by conversion into silver chloride had a factor of 1·000. Mixtures (1), (2), (3), (4) were made from these by adding to 50 c.c. of the $M/10$-sodium carbonate 47·75 c.c., etc., of the hydrochloric acid in order to produce solutions of ratios 1·06, etc., as above. These were kept in tightly corked flasks. So many c.c. were taken as contained the equivalent of 2·2 c.c. of $N/10$-alkali [for example, of mixture (1) 4 c.c.] and made up to 100 c.c. with distilled water free from carbon dioxide. These solutions were all $0{\cdot}0022N$ with respect to alkali and 0·0021 to $0{\cdot}00196M$ with respect to carbonic acid. Measured amounts of phenolphthalein were added, and the samples matched against the Sörensen borate–hydrochloric acid standards. The results are given in the third row above. The curve for $C=0{\cdot}002$ should fall slightly above that calculated for $C=0{\cdot}001$; actually it is slightly below.

The connexion was then determined between p_H and R of sea-water, in which the value of R was accurately known. The same standard carbonate solutions were diluted with neutral sea-water instead of with distilled water.

Many experiments carried out with the view of depriving sea-water or sea-salt of its "uncompensated base" and leaving it in a neutral condition were not sufficiently successful to warrant the use of such water in investigating the effect of adding such small quantities of carbonates and hydrogen carbonates. An artificial brine was therefore made from the crystallised salts, which possessed the average composition given in Clarke's "Data of Geochemistry," but omitting the potassium salts and others present in such small amounts that they were likely to have a negligible effect on the

alkalinities. This water was tested for neutrality by means of rosolic acid, which gave a yellow colour quite indistinguishable from that of a standard neutral solution having $p_H = 7{\cdot}07$. The addition of 0·2 c.c. of $N/100$-hydrochloric acid and $N/100$-sodium hydroxide to this water (10 c.c.) produced a perceptible change of colour, showing that the brine contained no appreciable amount of hydrolysed salts or hydrion regulator.

The solutions were then made up from the standard carbonates and this salt water as before. To 10 c.c. were added eight drops of 0·1 per cent. phenolphthalein or six drops of 0·04 per cent. α-naphtholphthalein. The salt error of the former is about 0·2 in p_H, and that of the latter is the same to a sufficiently close approximation (Sörensen). The hydrion standards used for comparison were (1) the borate–hydrochloric acid mixtures of Sörensen, (2) the partly neutralised mixture of phosphoric, acetic, and boric acids, which were previously found by the author (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 463) to replace suitably the borate standards from $p_H = 8{\cdot}3$ to 8·0. The results are as follows:

$R=$	1·06	1·08	1·10	1·12
p_H found.....	8·1	8·3	8·35	8·3
p_H corrected for salt...	7·9	8·1	8·15	8·1

As in the case of the water without salt, there is practically no change in the alkalinities between $R = 1{\cdot}08$ and $R = 1{\cdot}12$.

This was the case also both in the fresh and salt solutions having $R = 1{\cdot}16$.

On the average, then, p_H is 8·9 in fresh water containing hydrogen carbonate and carbonate of these ratios and carbonic acid at a total concentration of about 0·002 mol., whilst it is 8·1 in salt water, which is identical with respect to alkali and carbonic acid. This effect might, of course, be referred to the less complete primary ionisation of the hydrogen carbonate and carbonate in the presence of so much salt, leading to a diminished hydrolysis. The experimental fact, however, in itself seems to involve biochemical and geochemical consequences, which will be considered after some results on the equilibrium with atmospheric carbon dioxide.

The question whether sea-water is or is not saturated with atmospheric carbon dioxide has been much discussed. Fox (*loc. cit.*) has made a most useful series of observations of the actual pressures of carbon dioxide in equilibrium with waters of varying salinity. The values of hydrion were not then fully available as at present. Obviously there is a relation between hydrion content and pressure of carbon dioxide, and, indeed, from the data

at present available it should be possible to calculate the latter from the values for hydrion, R, etc. There are still, however, difficulties in the way of doing this, except by empirical equations. Some simple experiments carried out in the spring of 1919 at Port Erin throw some light on this question. Pure air, taken from outside the laboratory, was bubbled through sea-water for periods varying from a few hours to twenty-four and twenty-seven. The value of p_H found in this water was always 8·1.

Numerous blank experiments were being made during this period on the sea-water freshly drawn, and the p_H values varied between 8·2 and 8·3. This alkalinity was preserved when the water was allowed to remain motionless for a day or more in the laboratory. Thus, the sea-water when exposed to a current of air gained carbon dioxide in every case, and this although the alkalinity was distinctly low for the time of year, since the surface water had been mixed with the lower layers and brought into better contact with the air by recent storms. The usual range in sea-water is from 7·95 to 8·35, but values below $p_H = 8·1$ are exceptional in the case of surface waters, although they have been found in the Skager Rack and off the coast of Norway.

According to the above experiments, all waters of higher alkalinity than $p_H = 8·1$, that is, nearly all surface waters, will gain carbon dioxide from the air. The experiment was repeated on the artificial sea-water, which was made up with carbonates so that p_H was 8·2. By saturation with a current of air, this was reduced to 7·9 or 8·1 as measured by different standard solutions and indicators. From the measurements of the neutral sea-water containing known amounts of alkali and carbonic acid, it is seen that $p_H = 8·1$ in salt water corresponds with a ratio of about 1·08, and therefore any sea-water containing less than $2·2/1·08 = 2·04$ millimols. of carbonic acid to 2·2 milli-equivalents of alkali should gain carbon dioxide from the air.

This result may be compared with a deduction from Fox's measurements of the absorption of carbon dioxide in salt waters of varying salinity and alkalinity. The "physically dissolved" carbon dioxide is expressed as c.c. of the gas "a" dissolved at different temperatures for each 0·01 per cent. of carbon dioxide in the air. Thus, for his highest salinity = 20 per cent. of chlorine, which is nearly equal to that of the artificial salt water of the present work, $pa = 3 \times 0·0875 = 0·2625$ c.c. per litre of water at $t = 16°$ and $p_{CO} = 0·0003$ atmosphere.

The carbon dioxide combined with alkali "b" is given for each milligram of alkali expressed as hydroxyl and for each pressure and temperature of carbon dioxide. At $t = 16°$ and $p_{CO_2} = 0·0003$

atmosphere, b is 1·18. Taking Fox's value of the total alkali = 40 milligrams of hydroxyl, or 2·35 milli-equivalents, the total carbon dioxide = 0·26 + (1·18 × 40) c.c.:

$$R = \frac{\text{equivalents alkali}}{\text{mols. of carbonic acid}} = \frac{40 \times 22{\cdot}4}{17 \times 47{\cdot}46} = 1{\cdot}11.$$

If the sea-water has a total alkalinity of 2·2 milli-equivalents, or 37·4 milligrams of hydroxyl, R becomes 1·05. The value of R in equilibrium with air is not greatly affected by changes of temperature; thus 1·11 at 16° becomes 1·09 at 12° and 1·115 at 18°.

Thus the direct experimental result is confirmed that, in a water of total alkalinity equal to 2·2 milli-equivalents, the lowest ratio and the highest acidity that is normally encountered in sea-water is only just in equilibrium with atmospheric carbon dioxide, and that in all other cases the water will gain carbon dioxide.

The surface waters of the sea gain carbon dioxide, not only from the air, but also by mixture with the subjacent layers in which low values of p_H are almost invariably found, and likewise by the decay of plants. It is apparently only the photosynthetic action of seaweeds, plankton, etc., which maintains alkalinities of more than 8·1 in the surface waters. There is no known inorganic chemical agency which is capable of doing this. At the same time, since the pressure of carbon dioxide in the sea becomes greater than that in the atmosphere at alkalinities below $p_H = 8{\cdot}1$, the alkalinity of surface waters cannot fall much below this point.

The alkalinity of bicarbonated fresh waters is also kept at about $p_H = 8$, but by a different chemical equilibrium. In these cases, the ratio R, as defined above, is 1·00, and this, from the curve already quoted, corresponds with $p_H = 8{\cdot}2$. Solutions which have the higher ratios found in sea-water, namely, 1·06 to 1·16, and contain quite an appreciable amount of carbonate, could not long exist in fresh water; they give a strong pink colour with phenolphthalein, as already determined, and would rapidly gain carbon dioxide from the air, and probably also in many cases deposit calcium carbonate or basic magnesium carbonates. The converse effect is best seen by noting the probable course of events when a fresh water of temporary hardness 11, consisting of hydrogen carbonates having the same total alkali concentration as the sea, becomes mixed with it. The static acidity would be greatly raised; thus, if the salt could be added to the original hydrogen carbonate, p_H would fall to 7·6. This was found by an experiment in which the calculated quantities of the standard carbonate and hydro-

chloric acid were added to the neutral sea-water and the colour given with α-naphtholphthalein was matched against a "mixed acid" alkali standard. By the mixture of equal volumes of the fresh water and sea-water, the alkalinity would assume an intermediate value, and one lower than that in normal surface waters, whilst the pressure of carbon dioxide would be correspondingly high, and carbon dioxide must be given up to the air or to other large quantities of water until R rises again to 1·05. It is quite possible that the higher acidities and pressures of carbon dioxide which have been observed everywhere below the surface are due mainly to this cause—the continued addition of bicarbonate waters —without any adequate opportunity of yielding up the excess of carbon dioxide from such immense masses of water. It may also be noted that were it not for the effect of salt in raising to such a high degree the acidity and pressure of carbon dioxide which correspond with a given proportion of alkali and carbon dioxide, the sea would contain much more carbon dioxide than it actually does. Thus, if it consisted of a dilute hydrogen carbonate solution, such as a hard water in equilibrium with the air, it would contain about 5·5 per cent. more carbon dioxide combined with the same quantity of alkali. Since the total carbon dioxide is about 50 c.c. per litre, every cubic metre of sea-water would contain 2·25 litres of carbon dioxide more than at present. The relative availability for plant life of the carbon dioxide in fresh and salt waters is a different question. As shown by Moore and his collaborators (*loc. cit.*), the flora of the sea can use the carbon dioxide of the hydrogen carbonate to a certain limit which approximately corresponds with the production of carbonate. Now, owing to the effect of the salt, sea-water in equilibrium with the air already has a ratio of 1·04 to 1·06; there is some carbonate present. The alkali present in fresh water in equilibrium with the air, and of almost the same alkalinity, is practically all as hydrogen carbonate. Therefore, in the fresh water of the same total alkalinity, for example, 2·2 milli-equivalents per litre, there is more carbon dioxide available before the carbonate point is reached. On the other hand, far more carbon dioxide can be abstracted from sea-water without an excessive rise of alkalinity. A sea-water of original ratio = 1·06 $\left(=\frac{1}{0{\cdot}945}\right)$ can, by abstraction of carbon dioxide, have R changed to 1·16 $\left(=\frac{1}{0{\cdot}862}\right)$, losing 8·7 per cent. of the original carbon dioxide, and still only have an alkalinity corresponding with $p_H = 8{\cdot}35$. A fresh water of original ratio = 1·00 can have this changed to $R = 1{\cdot}06$ by losing 5·5 per

cent. of the original carbon dioxide, but this changes the alkalinity to the high value corresponding with $p_H = 8{\cdot}7$.

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CXIII.—*The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Water–Acetone Mixtures.*

By GEORGE JOSEPH BURROWS.

IN a previous paper (T., 1914, **105**, 1260) the author recorded some experiments on the inversion of sucrose by acids in water–ethyl alcohol mixtures. It was there found that the rate of inversion at first decreased slightly as water was replaced by alcohol up to about 50 per cent. of alcohol, and then increased. It was concluded from the results that the catalytic activity of the acid was really greater in alcohol than in water, and that the addition of water had a depressing effect on the rate of hydrolysis. At the same time, the author was unable to explain the decrease in the rate of inversion which results from the replacement of water by alcohol up to 50 per cent. mixtures without assuming that the mixed solvents had some specific effect on the rate of reaction, and it was there suggested that this was due to a change in the fluidity of such mixtures, causing a variation in the rate of catalysis similar to that observed in conductivity.

In obtaining the results in that work, the reaction was treated as a unimolecular one, the concentration of the water being neglected. This assumption was made in view of the fact that even in a solution containing 75 per cent. of alcohol by volume the ratio of the number of molecules of water to molecules of sugar present at the commencement of the reaction was 45, so that the decrease in concentration of the water during the reaction was only 1/45 of its original value. In a 50 per cent. alcohol mixture the ratio was 91. Under these conditions, it was considered that the concentration of the water could be omitted from the equation and the reaction considered as unimolecular.

If, however, the concentration of the water is considered, the value of k_1, calculated from the bimolecular equation

$$k_1 = \frac{1}{t(w-b)} \log \frac{b(w-x)}{w(b-x)}$$

(where b and w are the number of gram-molecules of sugar and water respectively in the solution at the beginning of the reaction), is, of course, much smaller than the corresponding value of k obtained from

$$k = \frac{1}{t} \log \frac{b}{b-x}$$

In this case, the total concentration of water is considered to represent its mass as one of the active substances, irrespective of the fact that it is present in large excess and only a small fraction of the total concentration is used up during the reaction.

The difference between the values of k and k_1 is shown in the following table:

Sucrose (10 *per cent.*) *and* N/2-*Hydrochloric Acid at* 25·0°.

Alcohol (volume per cent.).	k.	k_1.
0·0	0·00219	0·0000427
16·7	0·00213	0·0000491
25·0	0·00204	0·0000519
40·0	0·00192	0·0000607
50·0	0·00176	0·0000667
60·0	0·00185	0·0000877
75·0	0·00208	0·0001603

It will be seen that whereas the values of k pass through a minimum for a certain mixture, the values of k_1 steadily increase.

It appeared of interest to see if similar results would be obtained in the case of ester hydrolysis, and with this end in view experiments have since been performed on the rate of hydrolysis of methyl acetate by hydrochloric acid. Owing to its effect on the equilibrium, alcohol could not be used as one of the solvents in this research, so that the experiments were performed in mixtures of acetone and water. Acetone undergoes change under the influence of the acid used in the hydrolysis, but it has been assumed that this has no effect on the rate of hydrolysis of the methyl acetate.

The acetone used in these experiments was dried over and distilled from calcium chloride. The methyl acetate was freed from acetic acid by means of sodium carbonate and was distilled from calcium chloride; it was neutral to litmus. The volume of the

solution was adjusted at the temperature of the experiment, which was 25° in every case. The acetone percentages given are by volume; thus 70 per cent. acetone was prepared by mixing seven volumes of acetone with three of water. In preparing a 5 per cent. solution of methyl acetate for hydrolysis by $N/2$-hydrochloric acid in 70 per cent. acetone, the following method was adopted: 10 c.c. of methyl acetate were diluted to 100 c.c. at 25° with 70 per cent. acetone (A), 20 c.c. of $5N$-hydrochloric acid were mixed with 46·7 c.c. of anhydrous acetone, and the mixture was diluted to 100 c.c. at 25° with 70 per cent. acetone (B). Equal volumes of (A) and (B) were then mixed in a dry flask and placed in a thermostat at 25°. The weights of water and acetone used in preparing the solutions were also determined, so that all concentrations can be expressed in terms of gram-molecular weights. The reaction was followed in the usual way by titrating 5 c.c. of the solution under investigation with baryta solution after different intervals of time, the increase in titre indicating the concentration of the acetic acid produced. At first the reaction was treated as unimolecular, and the values of k were calculated from the equation

$$k = \frac{1}{t\sqrt{4bn+1}} \log \frac{4bn+2nx(\sqrt{4bn+1}-1)}{4bn-2nx(\sqrt{4bn+1}+1)} \quad . \quad . \quad (1)$$

obtained by integrating $\frac{dx}{dt} = k(b-x) - k_2x^2$.

In this equation $n = \frac{b-\xi}{\xi^2}$, where ξ represents the amount of ester which actually undergoes hydrolysis up to the equilibrium, b is the initial concentration of ester, and x the amount hydrolysed in time t. It was found that the above equation gave values of k which were quite constant for any particular solution. However, in the case of a series of experiments in different water–acetone mixtures, it was found that as the water was replaced by acetone the value of k at first decreased and then increased.

Owing to the relatively small concentration of water in solutions containing a high percentage of acetone, it was then decided to calculate all results also from the equation for a bimolecular reaction. The equation used was that given by Griffith and Lewis (T., 1916, **109**, 69),

$$k_1 = \frac{1}{tA} \log \frac{A+y+2(K-1)x}{A-y-2(K-1)x} \cdot \frac{A-y}{A+y} \quad . \quad . \quad . \quad (2)$$

obtained by integrating $\frac{dx}{dt} = k_1(b-x)(w-x) - k_2x^2$,

where

k_1 = rate of hydrolysis,

k_2 = rate of esterification,

b = initial number of gram-molecules of methyl acetate in 1000 c.c. of solution,

w = initial number of gram-molecules of water,

x = number of molecules of ester decomposed in time t.

In equation (2),

$$y = (w + b)$$

$$A = \sqrt{(w+b)^2 + 4(K-1)wb}$$

and $$K = \frac{k_2}{k_1} = \frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acetic acid}} \times C_{\text{alcohol}}}$$ at equilibrium.

The values of both k and k_1 obtained in any solution were found to be constant. This is seen in tables I and II, which contain the results for the hydrolysis of 5 per cent. methyl acetate by $N/2$-hydrochloric acid in 80 and 90 per cent. acetone (by volume) respectively.

TABLE I.

80 *Per cent. Acetone.*

$b = 0{\cdot}6267$; $w = 10{\cdot}20$; $K = 5{\cdot}14$.

t.	x.	$k_1 \times 10^5$.	$k \times 10^4$.
0	—	—	—
48·5	0·0506	7·41	7·51
78·5	0·0819	7·44	7·79
111	0·1095	7·43	7·56
138	0·1314	7·34	7·44
168	0·1575	7·44	7·55
228	0·1992	7·32	7·40
258	0·2200	7·36	7·43
318	0·2592	7·47	7·52
401	0·2983	7·31	7·35
∝	0·4963		
	Mean ...	7·40	Mean 7·51

TABLE II.

90 *Per cent. Acetone.*

$b = 0{\cdot}6267$; $w = 4{\cdot}752$; $K = 8{\cdot}97$.

t.	x.	$k_1 \times 10^5$.	$k \times 10^4$
0	—	—	—
50	0·0636	19·77	9·35
85	0·0991	18·95	8·91
10	0·1262	19·35	9·08
140	0·1523	19·12	8·94
206	0·2018	18·91	8·80
263	0·2435	19·80	9·18
324	0·2695	19·34	8·94
400	0·2957	19·16	8·82
484	0·3192	19·63	9·00
∝	0·3608	—	—
	Mean ...	19·56	Mean 9·00

In table III is given a summary of results obtained for the hydrolysis of 5 per cent. methyl acetate by $N/2$-hydrochloric acid in different water–acetone mixtures. The value of b is 0·6267 in each case. The value of K was determined by ascertaining at the completion of the reaction the amount of acetic acid produced and then calculating the equilibrium constant. It was found that the numbers so obtained varied with the different solutions. This method of determining the conditions at equilibrium by analysing the solution actually used for the rate of hydrolysis is undoubtedly open to error, as a small amount of the volatile substances must escape each time the flask is opened to determine the concentration of acetic acid at each particular time. The amount lost in this way during a complete experiment would probably be sufficient to introduce an error into the value of C (acetic acid), and this might lead to quite a large error in the value of K. The variations in K are possibly due to a small error in the values of the concentrations of acetic acid found for the various solutions. At the same time, it has been found that a comparatively large difference in K produces only a small difference in the value of k_1. Thus the mean value of k_1 for a solution containing 90 per cent. of acetone is found to be 19·56 when $K = 8·97$ and 18·7 when K is taken as 5, the approximate value found in the other solutions.

In the latter case, however, the numbers obtained for k_1 decrease regularly, whereas if the experimental values of K are taken there is no such decrease. For this reason, it has been decided to employ the values of K actually found, although it is realised that the variation in its value for the different solutions may be due, in part at least, to the method of determination.

In the following table, the values under k are calculated from equation (1), those under k_1 from equation (2).

TABLE III.

Methyl Acetate (5 *per cent.*) *and* N/2-*Hydrochloric Acid.*

Acetone (volume per cent.).	Gram-molecules of acetone per litre.	w.	K.	$k_1 \times 10^5$.	$k \times 10^4$.
0	0	52·32	5·40	2·76	13·58
20	2·665	42·46	5·10	3·03	12·28
40	5·39	32·08	4·38	3·38	10·33
60	8·10	21·23	4·47	3·86	7·91
70	9·42	15·72	4·51	4·56	7·05
80	10·66	10·20	5·14	7·40	7·51
90	11·84	4·752	8·97	19·56	9·00

It will be seen that the value of k_1 increases regularly as water is replaced by acetone as solvent. The values in the sixth column

under k, however, at first decrease as water is replaced by acetone and then increase.

A similar result was obtained for the hydrolysis of 2·5 per cent. methyl acetate by $N/10$-hydrochloric acid. Owing to the small amount of methyl acetate actually present at equilibrium, the value taken for K for each of the solutions in this series was the value found in the corresponding solution with 5 per cent. methyl acetate and $N/2$-hydrochloric acid.

TABLE IV.

Methyl Acetate (2·5 *per cent.*) *and* N/10-*Hydrochloric Acid.*

In all cases, $b = 0{\cdot}3133$ gram-molecules per litre.

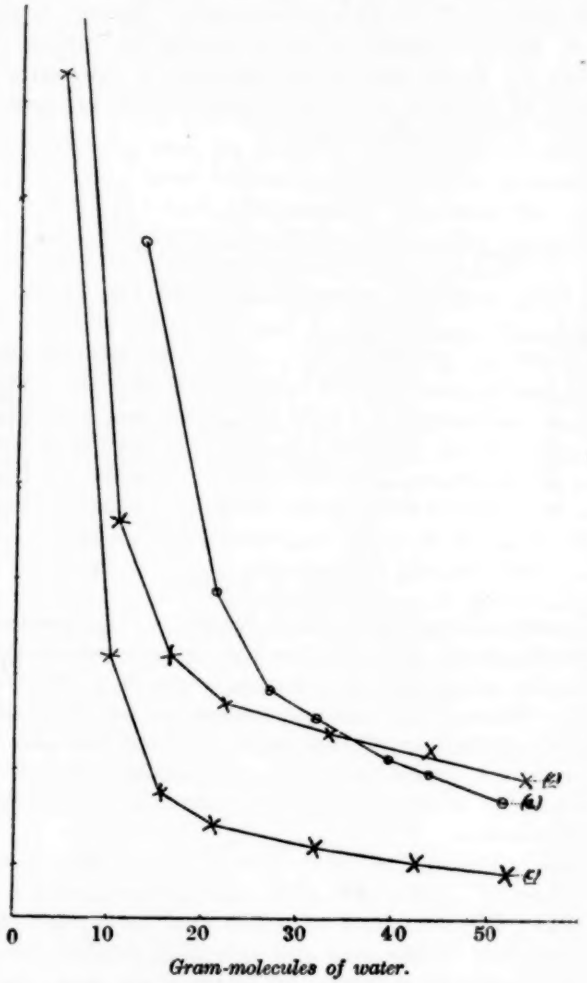
Acetone. Per cent.	Gram-molecules of acetone.	w.	$k_1 \times 10^4$.	$k \times 10^4$.
0	0	54·00	4·78	2·60
20	2·73	43·97	5·40	2·39
40	5·53	33·44	5·76	1·90
60	8·31	22·26	6·40	1·42
70	9·68	16·62	7·42	1·22
80	10·96	10·95	10·23	1·13
90	12·19	5·351	23·60	1·26

Discussion of Results.

If the values of k_1 given in tables III and IV are plotted against water concentrations, they are found to lie on a rectangular hyperbola. In the accompanying diagram, a graph is also shown for the results obtained for sucrose inversion given under k_1 in the table at the beginning of this paper. It will be seen that the three curves are similar in shape and indicate the decrease in catalytic activity of the acid which accompanies an increase in the water concentration.

Snethlage (*Zeitsch. physikal. Chem.*, 1913, **85**, 253), Acree (*Amer. Chem. J.*, 1912, **48**, 352), and Taylor (*Zeitsch. Elektrochem.*, 1914, **20**, 201) have advanced the theory that the undissociated molecule of the acid also acts as a catalyst, the activity of the undissociated molecule of hydrochloric acid varying for different reactions up to a value twice that of the hydrogen ion. In order to account for the present results according to this theory, it would be necessary to assume that $\frac{k_m}{k_{H'}}$ is about 20 (k_m being the activity of the undissociated molecule and $k_{H'}$ that of the hydrogen ion). Figures are not available for the degree of dissociation of hydrochloric acid in water–acetone mixtures, but in discussing the results obtained for the inversion of sucrose (*loc. cit.*), the author

gave values of a (HCl) deduced for water–alcohol mixtures. In the following table, the values observed for k_1 for sucrose inversion



(*a*) *Inversion of sucrose in water–alcohol.*
(*b*) *Hydrolysis of methyl acetate* (*N*/10-HCl) } *in acetone–water*
(*c*) „ „ „ (*N*/2-HCl)

(calculated as a bimolecular reaction) are compared with the total catalytic activity of the acid expressed as

$$k_m + k_{H'} = k_{H'}[a + 20(1 - a)],$$

the ratio $\frac{k_m}{k}$ being taken as 20.

TABLE V.

Alcohol (volume per cent.).	a (HCl).	$[a+20(1-a)]$.	$k_1 \times 10^5$.	$\frac{k_1 \times 10^5}{[a+20(1-a)]}$.
0	0·86	3·66	4·27	1·17
25	0·83	4·23	5·19	1·23
40	0·80	4·80	6·07	1·26
50	0·72	6·32	6·67	1·06
60	0·65	7·65	8·77	1·15
75	0·45	11·45	16·03	1·11

The numbers in the fifth column approximate to a constant. Although results cannot be calculated in this way for the hydrolysis of methyl acetate in water–acetone mixtures owing to lack of data, it is considered from the results obtained for k_1 in these solutions that if the value of a (HCl) were available, a similar constancy for $\frac{k_1}{a+x(1-a)}$ would be obtained for a value of x in the neighbourhood of 20.

It follows from the above that the activity of the catalyst in these mixtures can best be expressed by $k_1 = k_m + k_H$, when the ratio $\frac{k_m}{k_H}$ is considered to be about 20, but this value is not supported by results obtained by Snethlage and others for the catalytic effect of hydrochloric acid in other reactions.

The shape of the curves in the diagram suggests that in the mixtures investigated the variation of the activity of the acid with the water content is approximately expressed by $k_1(w+m)=n$, where m and n are constants and k_1 the observed rate of hydrolysis in a solution containing w gram-molecules of water. An equation of this type is capable of various interpretations, but taken in conjunction with the marked decrease in k_1 with increase in water concentration for low values of the latter, it indicates that the water plays a very markedly anticatalytic rôle compared with the other constituents of the solution, that is, the value of the constant m must be very small compared with w. This may be interpreted (compare Lapworth and Fitzgerald, T., 1908, **93**, 2168) as being due to the conversion of active, free hydrogen ions to inactive ions by the solvent, the effect of the water in this respect being far greater than that of the acetone. Or it may be interpreted as indicating that the reactive substance in ester hydrolysis is a complex between the ester and water, which is readily dissociated by the excess of water in the solution (Griffiths and Lewis, *loc. cit.*). It may also be interpreted as representing the dissociating effect of the solvent on a complex between the ester and the catalyst, which is considered to be the reactive

substance. Such a complex may either be dissociated by the solvent into the original substances or else hydrolysed by the water into the final products of hydrolysis. For the concentrations usually employed in hydrolysis the amount of this complex is very small owing to the high dissociating power of the water. As the latter is replaced by acetone or other liquid the dissociating power of the medium is decreased and the concentration of the complex is increased, so that the observed rate of hydrolysis is also increased. In any of the above cases it is possible to assign a small value to the term m, which really represents the relatively small power of the other constituents of the solution of converting an active substance into one which is inactive in catalysis. The following discussion is independent of the nature of m; it is concerned rather with its magnitude. We will assume that it is simply a function of the concentration of the other variable in the solution, namely, acetone. If we substitute in the equation $k_1(w+m)=n$ the values of k_1 and w in table III for solutions containing (*a*) 52·32 gram-molecules of water and no acetone, and (*b*) 4·752 gram-molecules of water and 11·84 of acetone, we obtain the value $m=0{\cdot}22$ (in terms of 1 gram-molecule of acetone in the solution). Substituting this value for the other solutions, the following results are obtained.

TABLE VI.

Acetone.	Acetone × 0·22	w.	$k_1 \times 10^5$.	$n=k_1(w+0{\cdot}22\times\text{acetone})$.
0·0	—	52·32	2·76	144
2·665	0·59	42·46	3·03	130
5·39	1·19	32·08	3·38	112
8·10	1·78	21·23	3·86	89
9·42	2·07	15·72	4·56	81
10·66	2·35	10·20	7·40	93
11·84	2·60	4·752	19·56	144

The numbers in the last column pass through a minimum value, and vary in a similar manner to the values under k in table III. Furthermore, for any small value of m in the equation $k_1(w+m)=n$, the values of n will be found to vary as in table VI. The similarity between the variations of k in table III and n in table VI appears to justify the use of the equation for a unimolecular reaction in mixtures such as those used in this work, in which the total concentration of water varies considerably in the different solutions. It would appear that any specific effect of the solvent on the rate of hydrolysis, other than that due to its dissociating power, is more directly shown by disregarding the change in the concentration of the water in the different solutions. It is considered that the minimum value obtained for k (or n) has a definite meaning. It is interpreted as indicating a specific influence of these mixtures on the rate of catalysis, similar to that

observed in the conductivity of certain electrolytes dissolved in them, or in the fluidity of the mixtures themselves. The solution of either alcohol or acetone in water is accompanied by contraction, and it is considered that the condensed state of such a mixture has a retarding influence on catalysis.

Summary.

The rates of hydrolysis of methyl acetate by $N/2$- and $N/10$-hydrochloric acid have been measured in various water–acetone mixtures. The velocity constants have been calculated according to both unimolecular and bimolecular equations, the reverse reactions being considered in both cases.

It has been found that if the total water concentration is taken as representing its active mass, then the rate of hydrolysis increases as water is decreased in the mixtures throughout the series. The results obtained approximate to $k_1 = k_m + k_{H'}$ if $\frac{k_m}{k_{H'}}$ is taken as 20 (approximately). The variation of k_1 with water concentration indicates the anticatalytic function of the latter, and if the values of k_1 are corrected for this effect the numbers so obtained are found to vary in a manner similar to those obtained by using the ordinary unimolecular equation, and pass through a minimum value for a certain mixture. This minimum is considered to have a definite meaning, representing a retarding influence of such mixtures on catalytic reactions.

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CXIV.—*The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides. Part II.*

By DAVID RUNCIMAN BOYD and MISS DORIS FELTHAM THOMAS.

A PREVIOUS communication (Boyd and Marle, T., 1914, **105**, 2117) contained an account of experiments on the combination of ethylene and propylene oxides with the sodium derivatives of a variety of phenols. The nature of the reaction investigated is indicated by the equation

$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>O + C_6H_5\cdot ONa + xC_6H_5\cdot OH =$$

$$\begin{matrix}CH_2\cdot O\cdot C_6H_5\\ |\\ CH_2\cdot OH\end{matrix} + C_6H_5\cdot ONa + x - 1C_6H_5\cdot OH.$$

From the results of these experiments, the conclusion was drawn that combination probably, in the first instance, takes place between the phenoxy-ion and the olefine oxide molecule, thus:

$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>\!O + R\cdot O' = \begin{matrix}CH_2\cdot OR\\ |\\ CH_2\cdot O'\end{matrix};$$

the initial additive product afterwards reacting with the excess of phenol to give a glycol aryl ether and a new phenoxy-ion,

$$\begin{matrix}CH_2\cdot OR\\ |\\ CH_2\cdot O'\end{matrix} + R\cdot OH = \begin{matrix}CH_2\cdot OR\\ |\\ CH_2\cdot OH\end{matrix} + R\cdot O'.$$

A comparison of the values for the velocity constant of the reaction with different phenols indicated that the speed of combination diminished with increase in the acidity of the phenol, and the suggestion was made that a certain analogy exists between the two reactions

$$C_6H_5\cdot O' + H^{\cdot} = C_6H_5\cdot OH$$

and

$$C_6H_5\cdot O' + \begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>\!O = C_6H_5\cdot O\cdot CH_2\cdot CH_2\cdot O'.$$

In other words, where the tendency for a phenoxy-ion to change into undissociated phenol is great, the speed of combination of the phenoxy-ion with the ethylene oxide molecule should be relatively high, and vice versa. The data available at the time, however, with regard to the relative acidities of different phenols were comparatively few.

An investigation of the extent to which the sodium derivatives of alkyl substituted phenols are hydrolysed in aqueous solution was afterwards carried out by one of us (T., 1915, **107**, 1538), and it then became possible to consider in more detail the relationship existing between the acidity of a phenol and the speed with which its sodium derivative combines with ethylene oxide. As a result, certain regularities with regard to the behaviour of ortho-substituted phenols came to light, and it appeared desirable to extend the observations so as to confirm, if possible, the generalisations which had suggested themselves. The present paper therefore includes experimental data for the velocity constants of three additional alkyl substituted phenols, namely, *o*-4-xylenol, *m*-6-xylenol, and mesitol. In all, results for eighteen phenols are dealt with. The facts are summarised in the accompanying diagram, where the velocity constants for the ethylene oxide reaction are plotted against the values for the percentage of hydrolysis of the sodium phenoxides in aqueous solution. A reference to this diagram will show that the velocity constants for phenol and

its meta- and para-substitution products lie approximately along a straight line, whilst the constants for the alkyl substituted phenols containing one alkyl group in an ortho-position lie approximately on a second straight line which runs nearly parallel with the first and some distance below it.

It appears, therefore, that whilst in general the speed of the ethylene oxide reaction increases approximately in proportion to the degree of hydrolysis of the sodium phenoxide, a retarding influence makes itself felt in those cases where an ortho-placed alkyl group is present in the phenol molecule. This retarding influence, it will be observed, is superimposed on the factor which in the main determines the speed of the reaction. It becomes apparent only as the result of such an analysis of the phenomena as is here suggested. A comparison of the actual magnitude of the velocity constant for phenol with that of the constant for any of the alkyl ortho-substituted phenols reveals no such retardation. Thus thymol, in the molecule of which an *iso*propyl radicle is present in the ortho-position to the hydroxyl group, has a velocity constant one and a half times as great as that of phenol. Mesitol, with two ortho-placed methyl groups, has a constant nearly twice as great as that of phenol. None the less, the retarding influence of the ortho-placed alkyl groups is operating in both instances. The case of mesitol is of particular interest in this connexion. Since in mesitol two ortho-placed methyl groups occur, the retardation might be expected to be more pronounced than in cases where only one such group is present. A consideration of the diagram shows that this anticipation is fully borne out by the experimental results.

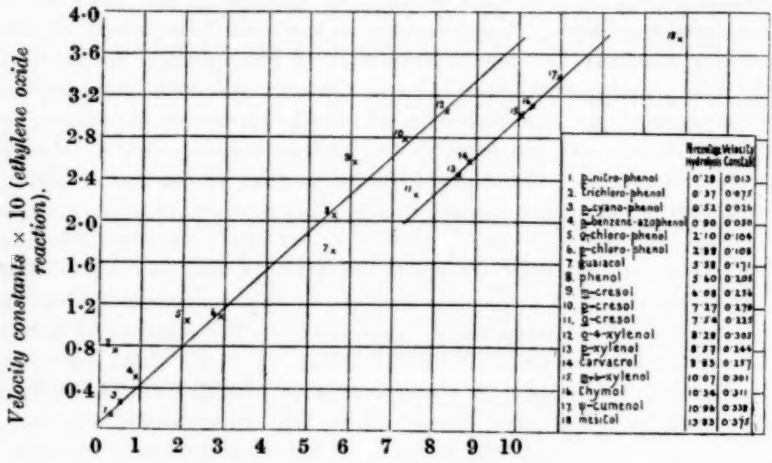
On the other hand, the position of the *o*-chlorophenol constant, and more especially of that for 2:4:6-trichlorophenol, indicates that negative substituents—or at least chlorine atoms—in the ortho-position act in an exactly opposite way, the velocity of combination being accelerated by their presence; and it is noteworthy that just as two ortho-placed alkyl groups cause a very pronounced retardation of the speed, so two ortho-placed chlorine atoms have an accelerating effect much more powerful than that due to a single chlorine atom.

Whilst it is natural to attribute to steric hindrance the retarding influence of the ortho-placed alkyl groups, a final decision on the question is not yet possible in view of the quite different effect produced by ortho-situated chlorine atoms. Further experimental evidence is also required to decide whether the accelerating influence of the chlorine atom should be ascribed to its residual affinity or to its polar quality. In the meantime, it may be pointed out that in the case of guaiacol, which contains an ortho-

situated group of ill-defined polar character, the velocity constant lies some distance above the line for phenols containing ortho-groups of well-marked positive type.

Experimental.

The velocity constants for *o*-4-xylenol, *m*-6-xylenol, and mesitol were determined at 70·4° in 98 per cent. alcohol according to the method previously described (T., 1914, **105**, 2117). It was found necessary to employ a mixture of light petroleum with ether (1 : 1) in separating glycol *m*-6-xylenyl ether from unchanged *m*-6-xylenol, since this phenol is not completely extracted from an ethereal



Percentage hydrolysis of sodium phenoxides in aqueous solution at 25°.

solution by repeated shaking with aqueous potassium hydroxide. The same method had to be employed in the case of the mesityl ether.

Summary of Results.

	Percentage yield of glycol ether.			$\frac{1}{t}\log\frac{100}{100-x}$.
o-4-Xylenol.	2 hours.	1 hour.	Maximum.	
	75·3	51·0	98·5	0·3050
	75·1	—	—	—
m-6-Xylenol.	2 hours.	1½ hours.	Maximum.	
	74·5	58·5	98·9	0·3005
	74·8	—	—	—
Mesitol.	2 hours.		Maximum.	
	82·3	—	99·0	0·3745
	81·8	—	—	—
	82·5	—	—	—

Glycol o-*xylyl ether*, $C_8H_9{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is a colourless oil boiling at 159°/18 mm. Its p-*nitrobenzoate* crystallises from alcohol in pale yellow plates melting at 225°:

0·1518 gave 6·5 c.c. N_2 (moist) at 23° and 762 mm. N = 4·82.
$C_{17}H_{17}O_5N$ requires N = 4·62 per cent

Glycol m-*xylyl ether*, $C_8H_9{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, was obtained as a white solid, which, after recrystallisation from light petroleum, melted at 57°:

0·1621 gave 0·4289 CO_2 and 0·1252 H_2O. C = 72·16; H = 8·58.
$C_{10}H_{14}O_2$ requires C = 72·23; H = 8·51 per cent.

Glycol mesityl ether, $C_9H_{11}{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, separates from light petroleum in glistening, white crystals which melt at 60°:

0·1556 gave 0·4196 CO_2 and 0·1263 H_2O. C = 73·54; H = 9·02.
$C_{11}H_{16}O_2$ requires C = 73·25; H = 8·97 per cent.

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CXV.—*Molecular Refractivity of Cinnamic Acid Derivatives.*

By ERIC WALKER and THOMAS CAMPBELL JAMES.

THE work of previous investigators has shown that the molecular refractivity of organic compounds is affected to a slight extent by constitutive influences within the molecule. In this investigation we have determined the amount of variation produced by change of constitution in a series of closely allied derivatives of cinnamic acid, and the results are tabulated below:

	$[M]_C$.	Difference.	$[M]_D$.	Difference.
α-Chlorocinnamic acid	50·24	—	50·96	—
α-Chloro*allo*cinnamic acid	49·00	1·24	49·59	1·37
Ethyl α-chlorocinnamate	58·33	—	58·98	—
Ethyl α-chloro*allo*cinnamate...	57·61	0·72	58·19	0·79
α-Bromocinnamic acid	52·90	—	53·52	—
α-Bromo*allo*cinnamic acid	52·34	0·56	53·06	0·46
Ethyl α-bromocinnamate	60·85	—	61·51	—
Ethyl α-bromo*allo*cinnamate...	60·54	0·31	61·14	0·37
β-Bromocinnamic acid	51·98	—	52·61	—
β-Bromo*allo*cinnamic acid ...	51·53	0·45	52·10	0·51
Dibromocinnamic acid	58·94	—	59·64	—
Dibromo*allo*cinnamic acid ...	—	—	—	—
Allyl α-chlorocinnamate.....	62·13	—	62·82	—
Allyl α-chloro*allo*cinnamate ...	60·52	1·61	61·08	1·74

An examination of the above figures confirms Brühl's observation that the more stable isomeride has the higher molecular refractivity, and shows also that, in the α-substituted compounds, the difference decreases with increase of molecular weight. It is also seen, from a consideration of the bromo-acids, that the α-substituted acid has a greater refractive power than the β-substituted acid.

Experimental.

(a) *Refractivity Measurements.*

Materials.—The acids and esters used in this investigation were all specially prepared, and the greatest care was taken to use only highly purified specimens for refractivity measurements. Details of new preparations are given at the end of the paper.

The solvent used for the acids was ethyl alcohol, rendered absolute by distilling the 99·8 per cent. commercial product over lime and afterwards over metallic calcium.

Apparatus and Method.—The solutions of the acids were made up by direct weighing to determine their percentage composition. In all cases, approximately 5 per cent. solutions were employed. The esters were all liquids and were determined directly.

Densities were determined by means of a Sprengel-Ostwald pyknometer of about 5 c.c. capacity. The pyknometer was suspended in a thermostat kept at 25° (±0·05°) for about fifteen minutes. The following formula was used:

$$d_{4^\circ}^{25^\circ} = \frac{W'D}{W} - \frac{0{\cdot}0012(W' - W)}{W},$$

where $d_{4^\circ}^{25^\circ}$ = density of solution at 25°, referred to water at 4°,
W' = weight of solution filling pyknometer,
W = weight of water filling pyknometer,
D = density of water at 25° (0·997073).

Refractive indices were measured by means of a form of Pulfrich refractometer furnished with an ordinary thermostat. The temperature of the liquid in the cell could be maintained at 25° (±0·05°) for a considerable time.

The refractive index of each liquid was measured for the *C* and *D* lines.

The zero error of the refractometer amounted to +1′, and all readings were corrected for this. The temperature correction amounted to about one unit in the fifth place of decimals in the refractive index, and could therefore be neglected.

The refractive index of the alcohol used as solvent was deter-

mined several times during the course of the work. The following values were obtained:

$$n_C = 1{\cdot}35787,\ 1{\cdot}35784,\ 1{\cdot}35774.$$
$$n_D = 1{\cdot}35967,\ 1{\cdot}35967,\ 1{\cdot}35954.$$

The specific refractivity, r, of the solute was calculated by the formula

$$r = \left[\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}\cdot\frac{100}{p}\right] - \left[\frac{n_a^2-1}{n_a^2+2}\cdot\frac{1}{d_a}\cdot\frac{100-p}{p}\right],$$

where n and d are refractive index and density of the solution at 25°, n_a and d_a are the corresponding quantities for alcohol at 25°, and p is the percentage composition by weight of solution.

For the pure esters the formula

$$r = \frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$$

was employed.

In the tables which follow, p and d have the same significance as above, n_C and n_D denote the indices of refraction for the C and D lines respectively, r_C and r_D refer to the specific refractions, and $[M]_C$ and $[M]_D$ to the molecular refractions for these lines. In the column headed "solution," the number refers to the specimen of substance used, whilst the letters denote the various solutions made up from the same specimen.

TABLE I.

α-Bromocinnamic Acid.

Constants for alcohol: $d = 0{\cdot}7851$; $n_C = 1{\cdot}35787$; $n_D = 1{\cdot}35967$.

Solution.	p.	d.	$n_{C.}$	$n_{D.}$	$r_{C.}$	$r_{D.}$	$[M]_{C.}$	$[M]_{D.}$
1*a*	5·041	0·8069	1·36552	1·36742	0·2332	0·2351	52·94	53·37
2*a*	5·192	0·8076	1·36580	1·36780	0·2332	0·2364	52·94	53·66
2*b*	4·677	0·8053	1·36493	1·36691	0·2327	0·2358	52·83	53·53
					Means ...		52·90	53·52

TABLE II.

*α-Bromo*allo*cinnamic Acid.*

Constants for alcohol as in table I.

1*a*	5·330	0·8077	1·36555	1·36757	0·2310	0·2342	52·43	53·16
1*b*	4·824	0·8056	1·36483	1·36681	0·2304	0·2338	52·30	53·07
1*c*	5·248	0·8075	1·36547	1·36747	0·2304	0·2333	52·30	52·96
					Means ...		52·34	53·06

TABLE III.

α-Chlorocinnamic Acid.

Constants for alcohol as in table I.

Solution.	*p*.	*d*.	n_C.	n_D.	r_C.	r_D.	$[M]_C$.	$[M]_D$.
1*a*	5·190	0·8034	1·36686	1·36893	0·2754	0·2795	50·26	51·01
1*b*	4·984	0·8026	1·36645	1·36851	0·2751	0·2793	50·20	50·97
1*c*	5·136	0·8031	1·36673	1·36879	0·2755	0·2796	50·28	51·03
2*a*	5·469	0·8042	1·36724	1·36930	0·2751	0·2785	50·21	50·83
						Means ...	50·24	50·96

TABLE IV.

*α-Chloro*allo*cinnamic Acid.*

Constants for alcohol: $d=0·7851$; $n_C=1·35774$; $n_D=1·35954$.

1*a*	5·008	0·8021	1·36560	1·36758	0·2685	0·2716	49·00	49·57
1*b*	5·051	0·8024	1·36570	1·36767	0·2681	0·2711	48·93	49·48
2*a*	5·206	0·8024	1·36576	1·36776	0·2689	0·2725	49·07	49·73
						Means ...	49·00	49·59

TABLE V.

β-Bromocinnamic Acid.

Constants for alcohol as in table IV.

1*a*	4·877	0·8062	1·36489	1·36681	0·2296	0·2317	52·12	52·60
2*a*	4·512	0·8045	1·36426	1·36623	0·2284	0·2318	51·85	52·62
						Means ...	51·98	52·61

TABLE VI.

*β-Bromo*allo*cinnamic Acid.*

Constants for alcohol as in table IV.

1*a*	5·044	0·8061	1·36454	1·36649	0·2270	0·2295	51·53	52·10

TABLE VII.

Dibromocinnamic Acid.

Constants for alcohol as in table IV.

1*a*	5·205	0·8107	1·36412	1·36603	0·1926	0·1949	58·94	59·64

TABLE VIII.

Ethyl α-Chlorocinnamate.

d.	n_C.	n_D.	r_C.	r_D.	$[M]_C$.	$[M]_D$.
1·1719	1·56292	1·57054	0·2771	0·2802	58·33	58·98

TABLE IX.

*Ethyl α-Chloro*allo*cinnamate.*

1·1569	1·54597	1·55246	0·2737	0·2764	57·61	58·19

TABLE X.

Ethyl α-Bromocinnamate.

d.	n_C.	n_D.	r_C.	r_D.	$[M]_C$.	$[M]_D$.
1·3885	1·57685	1·58450	0·2386	0·2412	60·85	61·51

TABLE XI.

*Ethyl α-Bromo*allo*cinnamate.*

1·3713	1·56474	1·56973	0·2374	0·2398	60·54	61·14

TABLE XII.

Allyl α-Chlorocinnamate.

1·1702	1·56718	1·57483	0·2792	0·2823	62·13	62·82

TABLE XIII.

*Allyl α-Chloro*allo*cinnamate.*

1·1457	1·53563	1·54164	0·2720	0·2745	60·52	61·08

Preparations.

Ethyl α-chlorocinnamate, $C_6H_5\cdot CH{:}CCl\cdot CO_2\cdot C_2H_5$.

B. p. 161—162°/8 mm. D_4^{25} 1·172.

0·3467 required 1·621 c.c. *N*-$AgNO_3$. Cl = 16·60.

$C_{11}H_{11}O_2Cl$ requires Cl = 16·84 per cent.

*Ethyl α-chloro*allo*cinnamate.*

B. p. 157—158°/10 mm. D_4^{25} 1·157.

0·2985 required 1·392 c.c. *N*-$AgNO_3$. Cl = 16·54.

$C_{11}H_{11}O_2Cl$ requires Cl = 16·84 per cent.

Allyl α-chlorocinnamate, $C_6H_5\cdot CH{:}CCl\cdot CO_2\cdot CH_2\cdot CH{:}CH_2$.

B. p. 162—163°/11 mm. D_4^{25} 1·170.

0·3340 required 1·470 c.c. *N*-$AgNO_3$. Cl = 15·61.

$C_{12}H_{11}O_2Cl$ requires Cl = 15·93 per cent.

*Allyl α-chloro*allo*cinnamate.*

B. p. 171°/28 mm. D^{25} 1·146.

0·2841 required 1·258 c.c. *N*-$AgNO_3$. Cl = 15·70.

$C_{12}H_{11}O_2Cl$ requires Cl = 15·93 per cent.

From the above, it will be observed that the boiling points and densities of the *allo*-esters are always below those of the *trans*-form.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
ABERYSTWYTH. [*Received, August 15th*, 1919.]

CXVI.—*The Determination of Ignition-temperatures by the Soap-bubble Method.*

By Albert Greville White and Tudor Williams Price.

The soap-bubble method for the determination of ignition-temperatures was first described by McDavid (T., 1917, **111**, 1003). In the method as finally adopted, the experimental error is assumed to be less than ±3°, and the results obtained for the ignition-temperatures of the various gases tested are given as:

Coal gas–air	878°
Ethylene–air	1000
Hydrogen–air	747
Carbon monoxide–air	931
Petrol (fraction 0—80°)–air	995
Benzene–air	1062
Ether–air	1033

The method is said to eliminate, so far as is practically possible, the time factor. The temperature of ignition is taken to be that temperature to which the gaseous mixture must be heated by the application of a hot body, so as to cause instantaneous ignition. McDavid's results are very high in comparison with other recent determinations.

Finding it necessary to determine the ignition-temperatures of certain ether–air mixtures, the authors decided to use the apparatus described by McDavid on p. 1005 (*loc. cit.*).

The igniting coil was mounted between two binding screws fixed into a small wooden stand, and was kept at the requisite temperature by means of current drawn from a battery of accumulators. A variable resistance of nichrome ribbon formed part of the circuit, which was completed by means of a sliding contact-maker. The current was measured by means of a delicate ammeter reading to 0·01 ampere. The soap solution was prepared by dissolving sodium oleate in water with the addition of a little glycerol. In all the experiments in which ether was used the ether–air mixture was made by weighing the requisite quantity of ether into an exhausted aspirator, from which it was displaced later by means of mercury. It was found that the presence of mercury caused a slight change in the concentration of the solvent above it. The glass pipe from which the bubbles were blown was connected to the aspirator by means of a ground-glass joint, so that there was no possibility of change in the concentration of the ether due to absorption of the vapour by the leading tube, which was of glass. In the other experiments the vapour–air mixture was

made by weighing the requisite amount of liquid into an exhausted 15-litre aspirator, and was in this case displaced by means of water. The hydrogen–air mixture was made up by volume in the same apparatus.

Standardisation of Apparatus.

The coils were standardised as described by McDavid; the salts used were carefully purified and were kept in an exhausted desiccator over phosphoric oxide. Before use the salt was crushed and only minute fragments were placed on the coil. When these precautions were taken the standardisation could almost invariably be repeated to 0·01 ampere. The number of amperes necessary to keep the coil at such a temperature, that, when in a steady state, the salt was just melted, was taken to be the amperage necessary to heat the coil to the melting point of that salt. The melting points are given in table I, and are the same as given by McDavid, except in the case of lead chloride, which he did not use.

TABLE I.

Salt employed.	Melting point used.	Melting point given in "Chemist's Year Book" for 1916.
Potassium sulphate.....	1072°	1050°
Sodium chloride	800	820
Potassium iodide.....	687	705
Lead chloride	485	485

For comparison the figures supplied in the "Chemist's Year-Book" for 1916 are given. It will be seen that the difference between these and the figures used is by no means negligible; the figure for lead chloride was taken from this source. Every effort was made to wind the coils as uniformly as possible, but in almost every case it was found that patches rather hotter than the average could be found.

In Fig. 1 are given the standardisations of some of the coils. It will be noticed that these curves are not straight lines, as was that determined by McDavid in the case of the coil used by him, but have a distinct curvature.

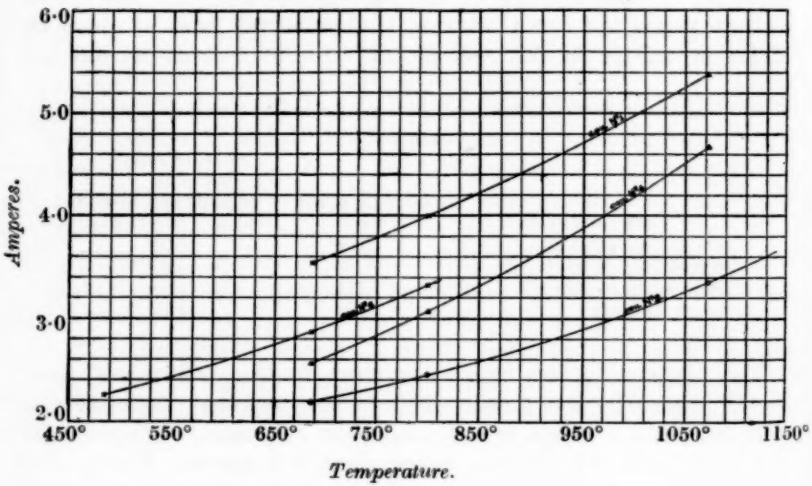
Standardisation of the Method.

Little work appears to have been done as regards standardising the soap-bubble method. McDavid used a soap-bubble 3·7 cm. in diameter, but no figures are given showing the effect of the size

of the bubble, or the place or the method of striking. All the standardisation undertaken in connexion with this method was done with coil No. 1, and most of it was carried out with ether–air mixtures, although in some cases hydrogen–air mixtures were also used, similar results being obtained. Throughout the work an attempt was made to keep the room temperature within 2° of 18°. For some time it was found exceedingly difficult to obtain accurate and steady ammeter readings, but the erection of a draught screen round the apparatus, and the gradual elimination of poor connexions, remedied these faults. It was also found that owing to the comparatively high currents used, the nichrome resistance

FIG. 1.

Showing the standardisation curves connecting the ammeter reading and temperature for various coils.



required frequent cleaning, and that the sliding contact-maker had to be silvered or fitted with a platinum contact.

So far as could be judged from the steadiness of the ammeter reading, no appreciable change in the temperature of any coil took place when it was brought into contact with a soap bubble blown with air. When using platinum-wound coils at the temperature necessary for the experiments, a very slight draught caused a distinct rise in the ammeter reading.

When determining an ignition-temperature the amperage was taken at which at least two ignitions were obtained out of three attempts, whilst 0·01 ampere below at least three successive failures to ignite were registered.

Size of Bubble and Place of Striking.

It was found that the size of the bubble used, and the place of striking, affected the results very appreciably, and various experiments were carried out in order to determine the magnitude of the variations due to these factors. The results of some of these tests are given in table II.

TABLE II.

	Mixture containing 7·5 per cent. of ether in air. Number of amperes necessary to ignite.			Mixture containing 12·5 per cent. of ether in air. Number of amperes necessary to ignite.		
Position of striking surface on bubble.	2·5 cm. bubble.	3·7 cm. bubble.	5 cm. bubble.	2·5 cm. bubble.	3·7 cm. bubble.	5 cm. bubble.
Struck at top	5·29	5·05	5·02	5·31	5·20	5·18
Struck at middle ...	5·29	5·05	5·02	5·32	5·20	5·18
Struck at bottom ...	5·41	5·08	5·03	5·43	5·22	5·20

On plotting the above results graphically, as in Fig. 2, it will be seen that the correct result appears to be about 0·01 ampere below the current necessary for the ignition of a 5 cm. bubble. Similar results were obtained using other concentrations of ether vapour in air. It scarcely appears to matter whether the bubble is struck at the top or middle, but striking at the bottom invariably gives a lower result. In practice, bubbles were always struck as near the middle as possible, and a 5 cm. bubble was always used. This size of bubble gave some little trouble owing to a tendency to give delayed ignitions and to burst before use, both effects being particularly noticeable with mixtures containing much ether. There was also a great tendency for the ether to leak through these bubbles. The method of striking was also found to have a great influence on the result, but it was found that a slow, but not too slow, approach of the coil to the bubble, or, even better, of the bubble to the coil, gave very consistent results. When the approach of the bubble was too slow, the ether pouring out through the soap film heated the coil so that the ammeter reading did not register its correct temperature.

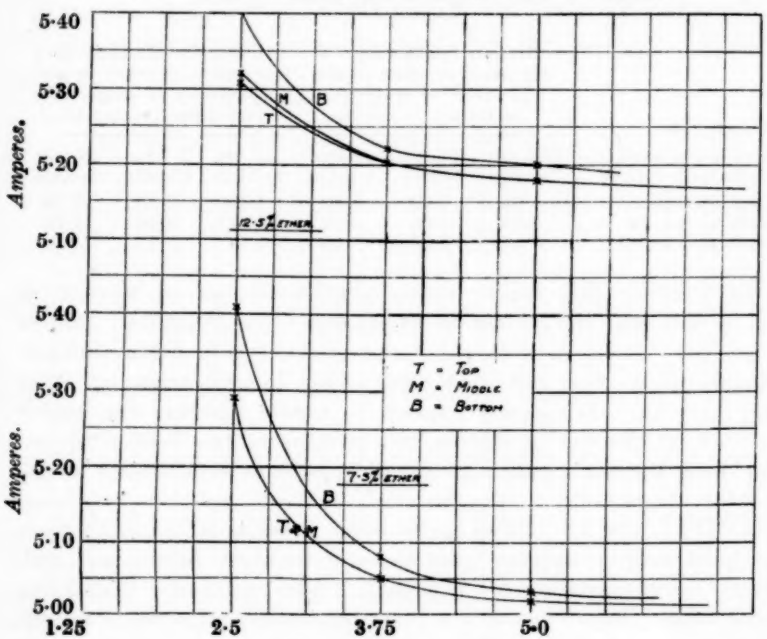
Time between Ignitions.

It was also found that a fair time had to elapse after one ignition before another could be attempted with any certainty of obtaining a trustworthy result. Even if a bubble was not ignited, heating of the coil took place, and a second bubble was very often

ignited at what was apparently the same temperature, unless time were given for the coil to cool. At least one minute had to be allowed between each attempted ignition, and often a longer time was necessary, the interval varying from coil to coil. It was also found that the time necessary for an adjustment of temperature

FIG. 2.

Showing how the current necessary to ignite a definite mixture varies with the size of bubble and position of striking.



due to change in the magnitude of the current flowing, varied greatly from coil to coil.

Changes in the Coil.

Even when experiments were carried out precisely as described in the above method, it was found that a coil gave different results for the same combustible mixture, even on the same day. Careful observation showed that these variations were generally all in one direction, and a connexion was soon traced between them and the standardisation of the coil used.

In table III are given the ignition-temperatures of a 4·9 per

cent. ether–air mixture determined with coil No. 1 at various times after standardisation.

TABLE III.

Within 20 minutes.	After 3 days' use.	After 3 weeks' use.	20 Minutes after re-standardising.
968°	985°	1040°	970°

It will be seen at once that the addition of salts to coil No. 1 lowered the ignition-temperature of the ether–air mixture as given by this method by 70°. Some such change might have been anticipated from the later work of Meunier (*Compt. rend.*, 1909, **149**, 924; 1910, **150**, 781). That this was not due to a change in the resistance of the coil can be seen from the fact that throughout the six months during which this coil was in use no point on the standardisation curve varied throughout a range of more than 0·02 ampere except on one occasion, when a variation of 0·03 was found. Precisely similar results were obtained in a test experiment on standardisation, even without washing off the salts used, as was invariably done in practice. A further investigation was then undertaken in order to discover how the ignition-temperature of a particular mixture varied with the treatment to which the coil was subjected.

The ammeter readings taken when using the untreated coil were converted into temperatures after the coil had been standardised by the use of salts. This was considered legitimate as every precaution was taken to ensure that the current–temperature ratio of the coil did not change with use. It was found that the newly-wound coil gave ignition at ammeter readings which increased continuously with time up to a steady value. The first ignition-temperature determined for a 27 per cent. hydrogen–air mixture, using coil No. 2 before treatment, was 760°. In a week's time the ignition-temperature had increased to 860°, but after this time no appreciable change in ammeter reading could be detected.

After standardisation or using salts it was found that a decided rise in the ignition-temperature had always taken place. This was invariably followed by an initially rapid fall, which decreased until a steady state was reached, the rate of decrease of temperature varying considerably with the nature of the coil, and its previous treatment. Thus, an untreated wire would take a very much longer time to reach a steady state than a recently treated or even a well washed wire which had once reached that state. For instance, the ignition-temperature of an ether–air mixture as determined by means of a platinum coil treated for the first time would probably take several days to become constant, whereas in

the case of a recently treated coil twenty minutes would be ample time.

Two hours after coil No. 2 was first treated with salts, the ignition-temperature of a 5 per cent. ether–air mixture as registered by this coil had fallen from 1068° to 1019°, whilst that of a 12 per cent. mixture, after its preliminary rise from 986°, had fallen to 1006° (see table IV). In both these cases the ignition-temperature of a 5 per cent. ether–air mixture appears to have fallen much more rapidly than that of a 12 per cent. mixture, as would be expected from the curves shown in Fig. 5.

In order to maintain a coil in the steady state, it was necessary to treat with salts occasionally. This caused a temporary rise in ignition-temperature, but it was only a matter of minutes before the steady state was re-established. The manner in which the ignition-temperature changed when no salts were added to a coil in the steady state can be seen from table III.

The temperature at which a steady state was attained after treatment was greater than without treatment except in the case of coils 1 and 2, which were of platinum. The variation was complicated in the case of the nichrome coil No. 3 by the fact that after being in the steady state for three days with a fairly continuous treatment with salts, a rather rapid fall in ignition-temperature became evident. When the fall became slower, the two points shown by asterisks in Fig. 5 were obtained, the one value, for a 5 per cent. ether–air mixture, being the mean of two readings 0·04 ampere apart obtained before and after the determination for a 12 per cent. ether–air mixture.

It will be noticed that in this case the ignition-temperature of a 5 per cent. ether–air mixture has fallen much more rapidly than that of a 12·5 per cent. mixture. This experiment was unfortunately interrupted by the breaking of the silica tube on which the coil was wound, making it impossible for the experiment to be carried to its logical conclusion; but it is at least possible that a flattened curve well below the original one (without salts) would have been obtained here as in the case of No. 1.

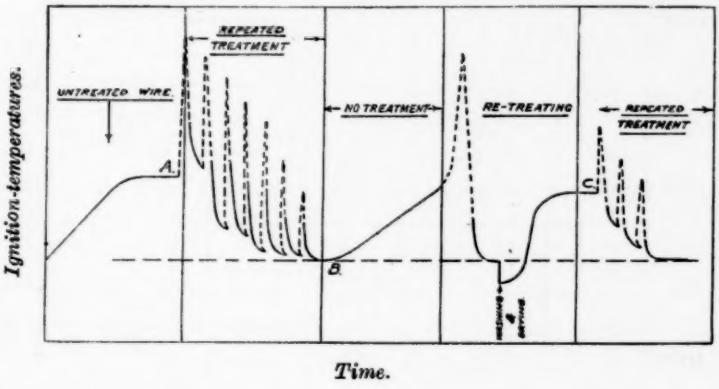
The upward change shown in table III could be made to take place even faster if the salts were washed from the coil and the coil used without treatment after drying. It was found that after eighteen hours' soaking of the coil in water, the ignition-temperature of a 27 per cent. hydrogen–air mixture as indicated by coil No. 1 fell from 787° to 771° and that of a benzene–air mixture fell from 1060° to 1056°. After sixty hours' soaking the result obtained for the hydrogen–air mixture was 773° and that for the benzene–air mixture 1056°. In all the above cases the ignition-

temperature was determined immediately after the drying of the coil was complete. During the course of three days after this preliminary fall, ignition-temperatures determined by this coil continued to rise, and at the end of this time, when the rise had become very slow, the figure found for the hydrogen–air mixture was 793° and that for the benzene–air mixture 1075°. Further results of a similar kind will be found later.

The effects of the changes considered above are shown in Fig. 3. It will be seen that consistent results are only to be expected under conditions corresponding with the three portions of the curve marked *A*, *B*, and *C*. Except where otherwise stated, results detailed later correspond with these steady states.

FIG. 3.

Showing diagrammatically the effect of various changes during the treatment of the wire on the ignition-temperatures registered by a coil.



Influence of the Material of the Coil.

McDavid (*loc. cit.*) states that the ignition-temperature of a 20 per cent. hydrogen–air mixture as determined by a Eureka wire coil is 9° to 30° lower than that obtained with platinum wire, and the statement is made that "The figures found by using platinum are higher than those obtained by using Eureka wire, indicating a catalysing effect in the case of the latter. It is, however, probable that both substances exert a catalytic influence." The results given above for coils Nos. 1 and 2 make it certain that the temperatures obtained are influenced very greatly by surface action in every case. It was accordingly decided to determine the ignition-temperatures of various ether–air mixtures using coils of different materials.

Coil No. 1 was made by winding platinum wire, 0·038 cm. in diameter, round a notched strip of mica.

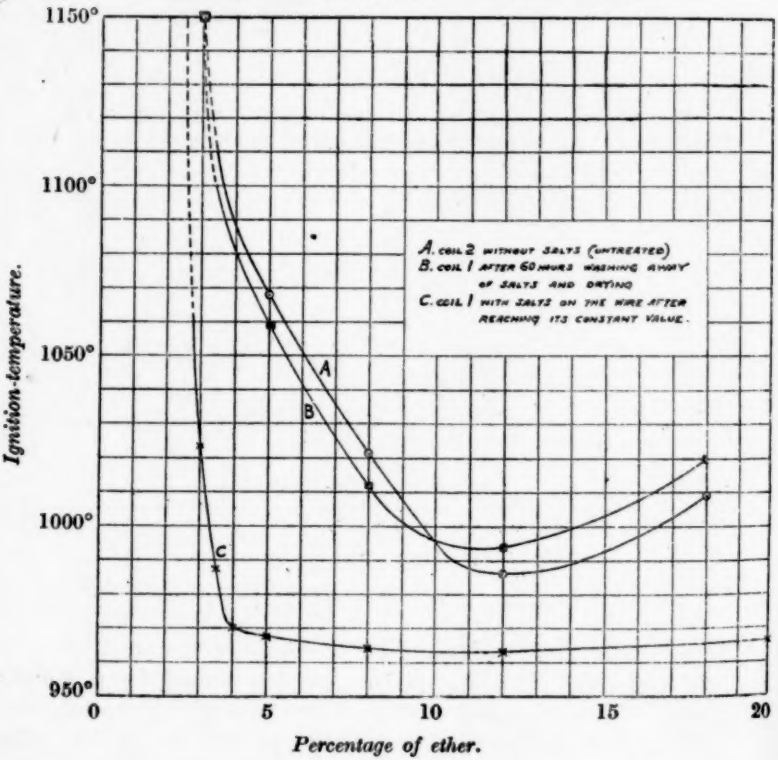
Coil No. 2 was a similar coil made with platinum wire, 0·025 cm. in diameter.

Coils Nos. 3 *and* 4 were made by winding nichrome wire, 0·05 cm. in diameter, round a narrow silica tube.

Coil No. 5 consisted of platinum wire, 0·025 cm. in diameter,

FIG. 4.

Showing the ignition-temperatures of various ether–air mixtures obtained with coils of platinum wire wound on mica.



wound inside a silica tube and having the platinum leads shielded by tubes of silica.

Coil No. 6 consisted of platinum wire of the same diameter as used in coil No. 5 enclosed in a uniform hard-glass tube with the leads safeguarded as for coil No. 5.

Fig. 4 gives the ignition-temperature curves obtained by plotting the results for various ether–air mixtures determined by means of

coils Nos. 1 and 2. It will be noticed that the curve obtained when coil No. 2 had attained a steady state before being treated with salts (or standardised) is close to that obtained when coil No. 1 had been allowed to attain a steady state after all the salts had been removed by prolonged washing and use. Curve *C* shows the ignition-temperatures obtained when coil No. 1 is treated with salts until the ignition-temperature obtained is constant. It differs from the other two curves inasmuch as the main body is very much flatter and that the difference in ignition-temperature between a 5 per cent. mixture and a 12 per cent. mixture of ether and air is very much less. The ignition-temperature of a 5 per cent. ether mixture as obtained from different curves on this diagram varies by 100°, whilst the maximum difference in the case of a 12 per cent. mixture is little more than 30°.

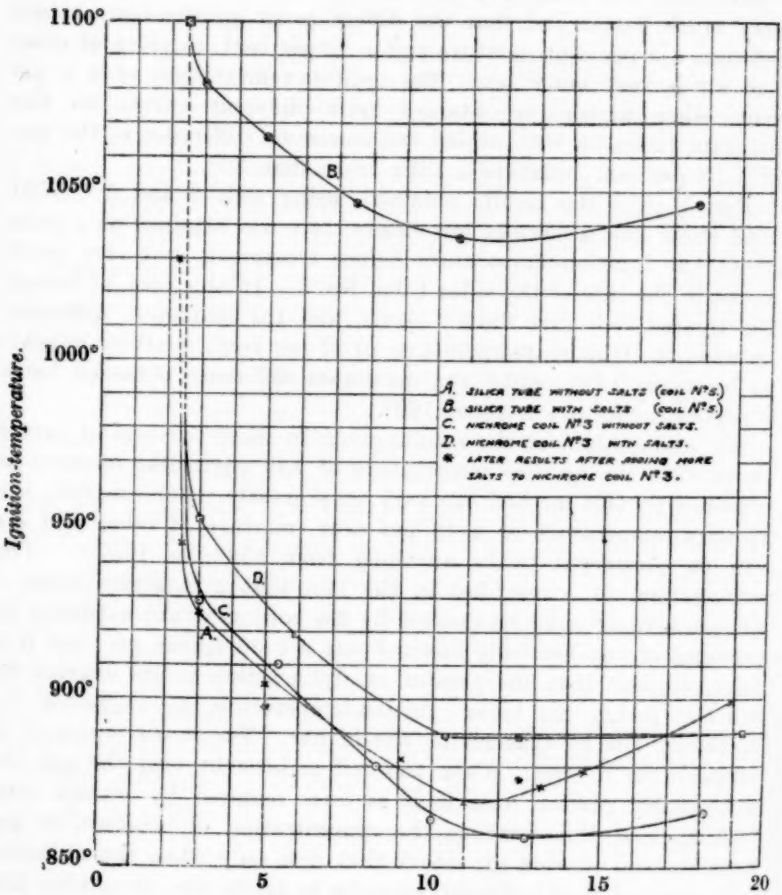
Fig. 5 gives the results obtained, using coils 3 and 5. With both these coils a more or less steady state was attained at a point above the ignition-temperature before treatment, and very much above in the case of the silica tube, No. 5. In this case, as before, the treated coils give flatter curves, and the maximum difference between the ignition-temperatures of 12 per cent. mixtures appears to be about 175°, whilst the maximum difference obtained for a 5 per cent. mixture is about 160°.

An examination of the results given in these two sets of curves shows that the ignition-temperature of any particular mixture as obtained by this method can vary very greatly. For example, the ignition-temperature of a 12 per cent. mixture of ether and air can be considered to be anything from 859° to 1035°. The explanation, of course, lies in the fact that a catalytic action—surface action—must be exerted by the coil, as would naturally be expected of any hot body inserted into a combustible gas; but it is fairly evident that the greater catalytic action is not exerted by the coil giving the lower ignition-temperature, as suggested by McDavid, but by that giving the higher. The *modus operandi* is probably as follows: When the coil is brought into the gas the combustible portion near it is at once removed by surface combustion, and this weakens the concentration of combustible gas near the coil to such an extent that it is only when the radiation from the coil is of sufficient intensity to ignite the gas outside this limited sphere that ignition occurs. This reasoning, which appears to be quite in keeping with what is known of the combustion of gases on surfaces, explains why in McDavid's experiments platinum gave a higher result than Eureka wire, and in the experiments described above, why, in the normal state, it gave results higher than either silica or nichrome when unaffected by salts. This

would also explain the reason why a coil had to be used for some time before attaining its maximum activity, as described in the standardisation of the apparatus.

FIG. 5.

Showing the ignition-temperatures of various ether–air mixtures obtained with coils of nichrome wound on silica and platinum inside silica.



Value of Method for obtaining Comparative results.

Although under any particular set of conditions the soap-bubble method is capable of giving results consistent to within ±5°, it will be seen that, giving as it does, such a range for the ignition-

temperature of any one gas–air mixture, it could scarcely be capable of giving the true ignition-temperature, particularly as surface action is bound to occur even when using the most indifferent material possible. It thus becomes a question as to whether even comparative results could be obtained by this method. It is seen from the curves given in Figs. 4 and 5 that those obtained with different coils occasionally cut one another, indicating that even comparative results could scarcely be obtained, assuming the experimental methods could be guaranteed accurate. As, however, the melting points of the salts used for standardisation purposes are not known to any great degree of accuracy,. and the standardisation curves are not straight lines, this evidence can scarcely be regarded as final. It was therefore decided to test several combustible mixtures, using the coils already made, in order to see if comparative results could be obtained by this method. Accordingly, the following mixtures were used, in addition to those mentioned previously:

1. A mixture of 27 per cent. of hydrogen in air.
2. A mixture of 5·7 per cent. of benzene in air
3. A mixture of 0·23 gram of light petroleum (b. p. 90—100°) per litre of air.
4. A mixture of 0·23 gram of light petroleum (b. p. 60—80°) per litre of air.

It was found to be impossible to obtain a definite ignition-temperature for a mixture of carbon disulphide and air or to ignite any mixture of alcohol and air or to obtain a reasonable size of bubble with mixtures of acetone and air. The results obtained are given in table IV.

In the course of these experiments it was noticed that it was easier to obtain an accurate result with hydrogen than with any of the other gases, and it was also very obvious that coils Nos. 5 and 6 gave results sooner and more accurately than the others. With any gases examined, when using these coils, it was easy to redetermine any figure to within 0·01 ampere, whilst with the other coils twice this variation was often found. Coils Nos. 1 and 2 scarcely changed at all during six months' use, but the result was far different in the case of coils wound over silica tubing. For example, three nichrome coils had to be rejected before a coil was found which would not change on heating, and this had to be kept at an exceedingly high temperature for some time before it reached this constant state. To test the comparative accuracy of the method, a second coil of platinum wound inside a hard glass tube was made and the ignition-temperature of a hydrogen–air mixture before treatment with salts determined.

TABLE IV.

Coil used.	Ignition temperature. Hydrogen–air, 27 per cent.	Light petroleum (b.p. 90–100°) –air, 0·23 gram per litre.	Light petroleum (b.p. 60–80°) –air, 0·23 gram per litre.	Benzene–air, 5·7 per cent.	Ether–air, 5 per cent.	Ether–air, 12 per cent.
No. 1. With salts	787	1035	1056	1060	968	963
After washing and use	793	1067	1075	1075	1059	994
No. 2. Without salts	860	1038	1040	1045	1068	986
With salts before constant	820	1040	1055	1060	1019	1006
No. 3. Without salts	—	—	—	—	911	859
With salts	—	—	—	—	928	888
No. 4. Without salts	764	1003	999	1025	—	—
With salts	773	1025	1016	1031	—	—
No. 5. Without salts	—	—	—	—	907	870
With salts	—	—	—	—	1064	1035
No. 6. Without salts	715	—	—	—	—	—
With salts	752	—	—	—	—	—
After washing	735	—	—	—	—	—

The result was quite satisfactory, as on standardisation it was found that the ignition-temperature obtained in this case was 712°, the result obtained using coil No. 6 being 715°. No similar tests were carried out with the other coils, as it was considered that in all cases except that in which a platinum coil was wound inside silica or glass, such a test would probably have been useless, as the ratio of the areas of the two constituent surfaces of the coil was bound to vary for every coil made. The results are interesting, as they show that the ignition-temperatures of two gaseous mixtures obtained by this method may not even be comparative when determined by two different coils. This was carefully tested in the case of the mixtures of the two varieties of light petroleum and air by using coil 4 without salts and coil 1 with salts. When coil No. 4 without salts was kept at 1001° and bubbles of the above mixtures were brought into contact with it alternately, in every case the mixture containing the light petroleum of lower boiling point ignited, whilst in only one trial out of five did the other one ignite. A similar experiment with coil No. 2 showed that the ignition-temperature of a mixture containing the light petroleum of lower boiling point was higher than that of the other as measured by this coil.

A similar result was obtained when dealing with a 5 per cent. mixture of ether in air, as in every case except when determined by coil No. 2 before treatment with salts, the ignition-temperature of this mixture was found to be lower than that of the light petroleum and benzene mixtures. In the case of the coil specified, however, the ignition-temperature found for a 5 per cent. mixture of ether in air was definitely higher than those of the other mixtures mentioned above.

In table V are given the maximum and minimum values obtained for the ignition-temperatures of certain of the mixtures used.

TABLE V.

W = Washed.
W.S. = Without salts.
S = After using salts.

Mixture used.	Maximum ignition-temperature observed.	Minimum ignition-temperature observed.	Difference.
Hydrogen (27 per cent.) in air	860° Coil 2 W.S.	715° Coil 6 W.S.	145°
Light petroleum (b.p. 90–100°) 0·23 gram per litre in air	1067 Coil 1 W.	1003 Coil 4 W.S.	64

TABLE V. (*continued*).

Mixture used.	Maximum ignition-temperature observed.	Minimum ignition-temperature observed.	Difference.
Light petroleum (b.p. 60–80°) 0·23 gram per litre in air	1075° Coil 1 W.	999° Coil 4 W.S.	76°
Benzene (5·7 per cent.) in air	1075 Coil 1 W.	1025 Coil 4 W.S.	50
Ether (5 per cent.) in air	1068 Coil 2 W.S.	907 Coil 5 W.S.	161
Ether (12 per cent.) in air	1035 Coil 5 S.	859 Coil 3 W.S.	176

When it is considered that the glass and silica coils were only used for the hydrogen and ether mixtures respectively, it will be seen that the results have an appreciable regularity as regards what is generally considered to be the catalytic order of the various substances concerned in the ignition. In this connexion, it must not be forgotten that the substance on which a metal coil is wound must affect the ignition-temperature obtained.

A comparison of the ignition-temperatures obtained, using coil No. 2 with and without salts, is also interesting. In the case of the hydrogen–air mixture and the 5 per cent. ether–air mixture, the treated coil gives appreciably lower results than the same coil without salts, but the reverse of this is true of all the other mixtures except light petroleum (b. p. 90—100°) and air when the ignition-temperatures are practically the same in the two cases.

On summing up, it will be seen that the only advantages which the method possesses appear to be those due to its convenience and rapidity in use. It was easy to find the apparent ignition-temperature of any mixture within less than an hour, and, using coils 5 or 6, it could often be done in half that time. The term "instantaneous ignition" is obviously used by McDavid to mean ignition without perceptible delay, but refined methods of time measurement would certainly show that different retardations occurred with different gas mixtures. Its disadvantages appear to lie in the fact that, so far as can be ascertained from these experiments, it cannot give the true ignition-temperature of any gas mixture, and that the results given by it can scarcely be utilised unreservedly even when only required for comparative purposes. Such results are fairly certain to be higher than the true ignition-temperatures, and not, as described by McDavid, lower. The accuracy of the method is also adversely affected by the fact that the exact melting points of the salts used are still a matter for controversy, and that the standardisation curve for any coil appears

from these experiments unlikely to be a straight line. The results are exceedingly dependent on draughts, as the method of estimating temperature is an indirect one. If the temperature of the coil falls during an experiment, due to any such disturbance in outside conditions, the ammeter reading, and hence the temperature indicated, becomes higher instead of lower, owing to the change in resistance of the platinum or other metal forming the heating coil. Any result obtained also seems to depend on the state of the surface causing ignition, as used and unused wire give different ignition-temperatures for the same gas mixture, and an examination under a good lens of wire that has been in use for some time shows it to have altered appreciably in appearance. Amongst its other disadvantages is that of limited applicability. It can only be applied to moist gases and to those which are more or less insoluble in water and can be obtained at a fair concentration in air at the ordinary temperature. For instance, it was found impossible to ignite a mixture of amyl acetate and air, made up at 20°, by this method. Another disadvantage lies in the fact that the least concentration of combustible gas at which ignition can be obtained by the soap-bubble method is much greater than that found by ordinary methods, which generally give results below 2 per cent. for ether–air mixtures. Thus the ignition-temperature of any fixed concentration of mixture cannot be determined by this method, as could also be judged from the obvious permeability of the soap film to some of the vapours used.

The results obtained during this investigation appear to indicate that the soap-bubble method of determining ignition-temperatures as described by McDavid gives values for the ignition-temperature which appear to be erroneous. A radical modification of the method could probably be made, however, which would give more satisfactory results. For instance, a soap-bubble of the mixture under examination might be introduced into a vertical tubular furnace, the bubble being shielded from radiation until at the desired spot. In this case, the results would be far more likely to be correct, as the temperature at which ignition took place would be known, and surface action would be partly eliminated.

Summary.

The soap-bubble method described by McDavid (*loc. cit.*) has been applied to determine the ignition-temperatures of certain mixtures of ether, benzene, light petroleum, and hydrogen with air. The conditions under which consistent results can be obtained are given.

After careful standardisation, the results given by this method were found to be affected by the physical state of the igniting surface and the nature of the material of which it was made; even the addition of small quantities of the salts used for standardisation purposes altered the results obtained. This seemed to show that the method could scarcely give the true ignition-temperature of a gas mixture. The ignition-temperature of a particular gas mixture as determined by two different coils often varied by more than 150°, and results appeared to indicate that the method was not strictly trustworthy even for comparative purposes.

In conclusion, the authors desire to express their thanks to Messrs. Nobel's Explosives Co., Ltd., for whom the work was carried out, and to Mr. Wm. Rintoul, Manager of the Research Section, for permission to publish the results, and to Mr. A. W. Sanderson for his kind assistance in carrying out some of the experimental work.

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CXVII.—*The Interaction of Chlorine and Hydrogen. The Influence of Mass.*

By DAVID LEONARD CHAPMAN and JOHN REGINALD HARVEY WHISTON.

AFTER investigating the precautions which must be taken in order to obtain trustworthy actinometric measurements of the velocity of the photochemical action of chlorine and hydrogen, Chapman and Underhill (T., 1913, **103**, 496) examined the influence of the concentration of hydrogen on this reaction. The determinations were made with mixtures containing small measured quantities of oxygen, and in the same series of determinations the concentrations of chlorine and oxygen in the mixtures were kept constant, whilst the concentration of hydrogen was varied. They found that "as the partial pressure of the hydrogen is increased from zero, the rate of formation of hydrogen chloride per unit volume of the mixture is at first almost proportional to the concentration of the hydrogen, but the ratio of partial pressure of hydrogen to velocity of interaction rises continuously in value as the propor-

tion of hydrogen is increased, and when the pressure of hydrogen has attained a definite value the rate of formation of hydrogen chloride becomes a maximum, and then, as the proportion of hydrogen is still further increased, the rate of interaction of chlorine and hydrogen falls very slowly."

It had previously been shown by Chapman and MacMahon (T., 1909, **95**, 959) that the sensitiveness of electrolytic gas at atmospheric pressure is approximately inversely proportional to the concentration of the oxygen it contains for proportions of oxygen varying between 0·08 and 1 per cent. by volume of the electrolytic gas.

These two results were interpreted by a theory advanced by Burgess and Chapman (T., 1906, **89**, 1433).

It was our intention to proceed with the investigation of the influence of the concentration of the chlorine on the rate of formation of hydrogen chloride. However, before we were able to complete our investigation, Bodenstein and Dux (*Zeitsch. physikal. Chem.*, 1913, **85**, 297) published the result that the reaction is of the second order in the case of a mixture containing equal volumes of chlorine and hydrogen and a small fixed proportion of oxygen. Our results mentioned above on the influence of the concentrations of hydrogen and oxygen were in the main confirmed by these authors.

It will be remembered that Wildermann (*Phil. Trans.*, 1902, **199**, 337) also found that the rate of formation of carbonyl chloride when a mixture containing equal volumes of carbon monoxide and chlorine was exposed to light of constant intensity was proportional to the square of the pressure of the interacting gases.

From Bodenstein and Dux's result and the facts that the rate of interaction is inversely proportional to the concentration of the oxygen and nearly independent of the concentration of the hydrogen (provided that this concentration is not too small), it can obviously be deduced that the rate of formation of hydrogen chloride when a fixed volume of electrolytic gas is exposed to homogeneous light of constant intensity is given approximately by the formula

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{k \,.\, I \,.\, [\mathrm{Cl_2}]^2}{[\mathrm{O_2}]},$$

in which k is a constant and I the intensity of the radiation.

Bodenstein and Dux confirmed the above formula with measurements made with mixtures containing unequal volumes of hydrogen and chlorine.

It may be stated immediately that we are unable to confirm the work of Bodenstein and Dux on the influence of the concen-

tration of the chlorine on the rate of the change. In fact, we find that, within wide limits of concentration of the interacting gases, the rate of formation of hydrogen chloride is given with fairly close approximation by the expression $\frac{k \cdot I \cdot [Cl_2]}{[O_2]}$, or, in other words, since $I \cdot [Cl_2]$ is proportional to the radiation absorbed per second, the hydrogen chloride formed is nearly directly proportional to the radiation absorbed and inversely proportional to the concentration of the oxygen.

The result embodied in the above expression for the rate of formation of hydrogen chloride in mixtures of compositions and pressures within the limits used in our experiments can be easily interpreted by the hypothesis of Chapman, Burgess, Gee, and Underhill. Briefly, the hypothesis in question postulates that the radiation is absorbed by the chlorine molecules. The absorbed energy in the molecules is gradually degraded. In the earlier stages, when the energy is still in a highly efficient form, the degradation is accomplished very rapidly and completely by the agency of oxygen and the other inhibitors. The degradation accomplished in this way is so complete that the resulting degraded energy is no longer capable of assisting the union of the chlorine and hydrogen. The absorbed energy in the chlorine molecules which escapes being degraded in the earlier stages by the inhibitors is transformed to lower forms of energy, which, although capable of activating the chlorine, are to a much less degree, and possibly not at all, degraded by the inhibitors. In other words, the life of an activated molecule is not shortened by the agency of the inhibitors.

Consider unit volume of the mixture of gases exposed to light of intensity I. The rate of accumulation of efficient energy will be $k_1 \cdot I \cdot [Cl_2]$, k_n being now and below taken to represent a constant.

The loss of efficient energy is due to two causes, namely, its degradation during the impacts of the chlorine molecules with oxygen molecules and the conversion of the chlorine molecules into the activated form. When, however, the proportion of oxygen to electrolytic gas is as high as 1 per cent. (as it was in all the experiments to be described below), the sensitiveness is almost one hundred times less than that of the purest electrolytic gas we could prepare, and therefore with such a large proportion of oxygen present, the loss of accumulated efficient energy must be almost entirely due to the first of the above-mentioned causes.

Now the number of impacts per second between chlorine molecules and oxygen molecules is given by the expression

$k_2 . [O_2][Cl_2]$. Further, if it be assumed that in the mean a constant proportion of the efficient energy is degraded during an impact of a chlorine molecule with an oxygen molecule, the degradation of energy during a single impact will be, in the mean, $k_3\epsilon$, ϵ being the mean efficient energy of a chlorine molecule after the steady state is reached.

The rate of loss of efficient energy will be the product of the loss during a single impact and the number of impacts per second, which is $k_2 . k_3 . \epsilon . [O_2][Cl_2]$.

Equating this to the rate of accumulation of efficient energy, we obtain $k_2 . k_3 . \epsilon . [O_2][Cl_2] = k_1 . I . [Cl_2]$, and therefore

$$\epsilon = \frac{k_1}{k_2 k_3} \cdot \frac{I}{[O_2]}.$$

Now if we make the probable assumption that the rate of formation of active chlorine molecules is proportional to the product of the concentration of the chlorine and mean efficient energy of a single molecule,* the number of active molecules formed per second should be

$$\frac{k_1 . k_4}{k_2 . k_3} \cdot \frac{I . [Cl_2]}{[O_2]},$$

but when the pressure of the hydrogen exceeds 15 cm., and possibly at much lower pressures, almost all the active molecules of chlorine combine with hydrogen (Chapman and Underhill, *loc. cit.*), and the rate of formation of hydrogen chloride becomes equal to the active molecules of chlorine produced per second and almost independent of the pressure of the hydrogen.

Therefore the number of molecules of hydrogen chloride formed per second is also given by the expression

$$\frac{k_1 . k_4}{k_2 . k_3} \cdot \frac{I . [Cl_2]}{[O_2]}.$$

That is, the hydrogen chloride produced is proportional to the radiation absorbed and inversely proportional to the concentration of the oxygen.

If, as we have reason to believe is the case, hydrogen is a weak inhibitor (Chapman and Underhill, *loc. cit.*), the expression for the rate of formation of hydrogen chloride molecules would become

$$\frac{k_1 . k_4}{k_2 . k_3} \cdot \frac{I . [Cl_2]}{[O_2] + k_5[H_2]},$$

* This assumption is equivalent to the assumption that the tendency of each quantum of efficient energy to change its form is independent of the concentration of the chlorine.

in which k_5 is a constant of small magnitude. Since in our experiments, however, the pressures of the hydrogen and the oxygen have been varied in the same ratio, our results are in equal agreement with both formulæ, and fail to distinguish between them.

Experimental.

Experiments with the Moist Gases.—The apparatus used was a form of Bunsen and Roscoe's actinometer, in which the pressure of the contained gas could be varied, very similar to that used by Chapman and Underhill. The precautions taken in making the measurements and to ensure purity of materials were the same as those observed by Chapman and Underhill.

The mixture of gas experimented with was electrolytic gas which contained about 1·3 per cent. of oxygen by volume. The sensitiveness of the mixture at a pressure of one atmosphere and half an atmosphere was measured, and the results are tabulated below.

Number of experiment.	Sensitiveness at one atmosphere.	Sensitiveness at half an atmosphere.
1.	1000	1029
2.	1000	973
3.	1000	1060

Accordingly, with the moist gases the total hydrogen chloride formed in unit time is almost independent of the pressure, whereas if Bodenstein and Dux's result were correct, the rate of formation of hydrogen chloride ought to be proportional to the pressure.

Experiments with the Dry Gases.—For these experiments, the apparatus was modified in one or two respects. The mixture of gases before use was confined in a gas-holder over sulphuric acid. The sulphuric acid which the holder contained was saturated with chlorine and boiled several times, and the gas-holder was so constructed that the sulphuric acid did not come into contact with the air of the laboratory. The actinometer was the same as that used in the experiments with the moist gases, with the exception that the index contained sulphuric acid and the insolation vessel was horizontal and contained anhydrous copper sulphate spread uniformly over the bottom of the tube to serve as an absorbent of the hydrogen chloride. The copper sulphate was carefully dehydrated in the insolation vessel and heated in a current of chlorine at about 300° for an hour. The internal diameter of the insolation vessel was 2·6 cm. The results are tabulated below.

Number of experiment.	Sensitiveness at one atmosphere.	Sensitiveness at half an atmosphere.	Sensitiveness at a quarter of an atmosphere.
1.	1000	963 936	755*
2.	1000	—	776*
3.	1000	944	—
4.	1000	—	758*
5.	1000	—	752*

* At this low pressure it is possible that many of the activated chlorine molecules lose their activity before making fruitful impacts with the hydrogen molecules (compare Chapman and Underhill, *loc. cit.*).

Bodenstein and Dux admit that inhibitors were gradually produced in the insolation vessel during an experiment, and these inhibitors would tend to increase the apparent order of the reaction. They claim to have eliminated the effect of these inhibitors by the method of conducting their experiments, but it seems to us most likely that the discrepancy between their results and ours is due to this cause.

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CXVIII.—*Auto-complexes in Solutions of Cupric Chloride and Cupric Bromide.*

By STEWART BYRON WATKINS and HENRY GEORGE DENHAM.

IN a paper by Donnan and Bassett (T., 1902, **81**, 939), the view is expressed that the changes in colour brought about in solutions of copper and cobalt salts by changes in concentration and temperature, as well as by the addition of certain other haloid salts, are to be attributed to the formation of complex anions, as exemplified in the following equations:

$$Cu^{\cdot\cdot} + 2Cl' + xCuCl_2 \rightleftharpoons Cu^{\cdot\cdot} + \left[\frac{Cl_2}{(CuCl_2)_x}\right]''$$

$$2K^{\cdot} + 2Cl' + xCoCl_2 \rightleftharpoons 2K^{\cdot} + \left[\frac{Cl_2}{(CoCl_2)_x}\right]''$$

the colour of the anions so formed differing essentially from the colour of the cupric and cobalt ions. Quantitative support to this theory was first afforded by Kohlschütter's migration experiments (*Ber.*, 1904, **37**, 1193), whilst the investigations of one of the authors (*Zeitsch. physikal. Chem.*, 1909, **65**, 64) have shown that in concentrated aqueous and alcoholic solutions of copper and cobalt haloid salts, the cations have a migration number which is distinctly negative. The present paper is an extension of the investigation, and deals with the effect of temperature and concentration on the migration number of the cupric ion.

The experimental method adopted was practically the same as in the former paper, and the results obtained are of the same order of accuracy. Experiments were nearly always carried out in duplicate, and the middle layer was repeatedly analysed.

Below are the experimental results:

TABLE I.

Copper Chloride in Aqueous Solution. Temperature, 35°.

Before electrolysis:	Expt. 1.	2.	3.	4.
Water, grams	13·6121	9·1827	7·931	2·1160
Copper, grams	0·3455	0·4368	1·0695	0·5273
Concentration in gram-mols per litre	0·25	0·75	2·1	4·0
After electrolysis:				
Cathode liquid, grams	36·0216	35·4874	41·2016	46·1836
Copper found in cathode liquid, grams	0·8176	1·4775	4·2870	7·5189
Voltameter Ag	0·2272	0·2718	0·2750	0·1994
Equivalent $Cu^{..}$	0·0669	0·0808	0·0810	0·0587
Copper on cathode	0·0735	0·0832	0·0252	nil.
Cuprous copper in solution	0·0604	0·0784	0·1368	0·1173
Cuprous chloride in solution	0·0941	0·1221	0·2126	0·1828
Cupric copper in solution	0·8112	1·3991	4·1702	7·4016
Cupric chloride in solution	1·7170	2·9605	8·8256	15·6942
Total salt	1·8111	3·0826	9·0382	15·8770
Water	34·2105	32·4048	32·1634	30·3066
Migration number	0·34	0·24	−0·06	−0·57

Temperature, 45°.

Before electrolysis:	Expt. 1.	2.	3.	4.
Water, grams	13·6131	9·1827	6·8970	8·1700
Copper, grams	0·3455	0·4368	0·9180	1·6600
Concentration in gram-mols. per litre	0·25	0·75	2·1	3·2
After electrolysis:				
Cathode liquid, grams	32·0180	41·1732	43·9082	48·4132
Copper found in cathode liquid, grams	0·6848	1·7113	4·5420	6·8680
Voltameter Ag	0·3659	0·3048	0·2611	0·3105
Equivalent $Cu^{..}$	0·1052	0·0898	0·0770	0·0915

TABLE I. (*continued*).

Copper Chloride in Aqueous Solution. Temperature, 45°.

After electrolysis :	Expt. 1.	2.	3.	4.
Copper on cathode	0·1161	0·0978	0·0322	nil.
Cuprous copper in solution ...	0·0942	0·0820	0·1217	0·1829
Cuprous chloride in solution	0·1467	0·1277	0·1896	0·2849
Cupric copper in solution.....	0·5906	1·6293	4·4203	6·6851
Cupric chloride in solution ...	1·2500	3·4460	9·3520	14·1500
Total salt	1·3967	3·5737	9·5416	14·4349
Water	30·6213	37·5995	34·3666	33·9783
Migration number	0·22	0·135	−0·01	−0·40

TABLE II.

Copper Bromide in Aqueous Solution. Temperature, 35°.

Before electrolysis :	Expt. 1.	2.	3.	4.
Water, grams	21·976	6·8659	2·2323	1·2527
Copper, grams	0·5036	0·3302	0·2246	0·2847
Concentration in gram-mols. per litre	0·36	0·76	1·6	3·6
After electrolysis :				
Cathode liquid, grams	42·5353	41·5343	48·6760	57·9704
Copper found in cathode liquid, grams	0·8739	1·6396	3·6298	7·3307
Voltameter Ag	0·0893	0·1891	0·1857	0·2000
Equivalent $Cu^{\cdot\cdot}$	0·0272	0·0558	0·0547	0·0589
Copper on cathode	0·0394	0·0908	0·0005	nil.
Cuprous copper in solution ...	0·0194	0·0207	0·1089	0·1177
Cuprous bromide in solution	0·0368	0·0467	0·2461	0·2660
Cupric copper in solution.....	0·8590	1·6189	3·5209	7·2130
Cupric bromide in solution ...	3·0200	5·6901	12·3752	25·3589
Total salt	3·0568	5·7368	12·6214	25·6249
Water	39·4785	35·7975	36·0546	32·3455
Migration number	0·32	0·16	0·05	−0·35

Temperature, 45°.

Before electrolysis :	Expt. 1.	2.	3.
Water, grams	10·7732	2·2323	1·2527
Copper, grams	0·2518	0·2246	0·2847
Concentration in gram-mols. per litre	0·35	1·6	3·6
After electrolysis :			
Cathode liquid, grams	40·8411	49·4290	52·5873
Copper found in cathode liquid, grams	0·7959	3·6765	6·6333
Voltameter Ag	0·2205	0·1673	0·1937
Equivalent $Cu^{\cdot\cdot}$	0·0651	0·0489	0·0570
Copper on cathode	0·1068	nil	nil
Cuprous copper in solution	0·0233	0·0977	0·1140
Cuprous bromide in solution	0·0526	0·2206	0·2576
Cupric copper in solution.....	0·7726	3·5788	6·5193
Cupric bromide in solution	2·7169	12·5821	22·9200
Total salt	2·7695	12·8027	23·1776
Water	38·0716	36·6263	29·4061
Migration number	0·19	−0·18	−0·88

TABLE III.

Copper Bromide in Ethyl Alcohol. Temperature, 35°.

Before electrolysis:	Expt. 1.	2.	3.
Alcohol, grams	10·3713	9·0477	5·8932
Copper, grams	0·1441	0·2517	0·5059
Concentration in gram-mols. per litre	0·21	0·43	1·3
After electrolysis:			
Cathode liquid, grams	13·3029	13·7986	16·7181
Copper found in cathode liquid, grams	0·1464	0·3244	1·0655
Voltameter Ag	0·1124	0·0985	0·1065
Equivalent $Cu^{"}$	0·0332	0·0300	0·0314
Copper on cathode	0·0151	0·0114	0·0176
Cuprous copper in solution	0·0512	0·0466	0·0452
Cuprous bromide in solution	0·1156	0·1052	0·1021
Cupric copper in solution	0·0952	0·2788	1·0203
Cupric bromide in solution	0·3345	0·9767	3·5871
Total salt	0·4501	1·0819	3·6892
Alcohol	12·8528	12·7167	13·0289
Migration number	−0·51	−0·60	−1·1

Temperature, 45°.

Before electrolysis:	Expt. 1.	2.	3.
Alcohol, grams	10·3713	9·0477	5·2739
Copper, grams	0·1441	0·2517	0·3822
Concentration in gram-mols. per litre	0·21	0·43	1·17
After electrolysis:			
Cathode liquid, grams	13·5570	14·0426	15·8708
Copper found in cathode liquid, grams	0·1495	0·3282	0·8582
Voltameter Ag	0·1033	0·0822	0·1229
Equivalent $Cu^{"}$	0·0305	0·0243	0·0362
Copper on cathode	0·0098	0·0103	0·0270
Cuprous copper in solution	0·0510	0·0382	0·0454
Cuprous bromide in solution	0·1152	0·0862	0·1025
Cupric copper in solution	0·0985	0·2900	0·8128
Cupric bromide in solution	0·3463	1·0038	2·8576
Total salt	0·4615	1·0900	2·9601
Alcohol	13·0955	12·9526	12·9107
Migration number	−0·77	−0·90	−1·35

Discussion of Results.

The boundary migration experiments described by Steele (*Zeitsch. physikal. Chem.*, 1902, **40**, 689) and by Donnan and Bassett (*loc. cit.*), supported by the quantitative migration experiments of Kohlschütter (*loc. cit.*) and of Denham (*loc. cit.*), have afforded considerable support to the theory of complex-formation in concentrated solutions of copper and cobalt salts. In Denham's experiments it was found that at 25° the migration number of

copper in a 5·29 solution of copper bromide reached the strikingly low value −0·39. This was interpreted by assuming that in such solutions complex anions of the type $[CuBr_4]''$, $[Cu_2Br_6]''$, etc., carried copper out of the cathode compartment. Thus, assuming that the equilibrium

$$Cu'' + CuBr_2 + 2Br' \rightleftharpoons Cu'' + [CuBr_4]''$$

lies almost wholly to the right, the migration number would be approximately zero, whilst if appreciable $[Cu_2Br_6]''$ ions were present, as demanded by the equilibrium

$$Cu'' + 2CuBr_2 + 2Br' \rightleftharpoons Cu'' + [Cu_2Br_6]'',$$

values less than zero would result.

The parallelism between the migration number and the colour of the solution is shown in table IV.

TABLE IV.

Copper Bromide in Water. Temperature, 25°.

Concentration.	u_n.	Colour.
0·106	0·445	bluish-green.
0·414	0·440	green.
1·690	0·069	brownish-green.
2·218	0·052	,,
3·187	−0·086	brown.
4·055	−0·159	deep brown.
5·288	−0·392	,,

On the other hand, many have sought an explanation of this colour-change in the hydration either of the dissolved salt or of the copper cation (notably Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 185; Jones and his pupils, *Carnegie Publ.*, No. 60; for complete bibliography, see *Zeitsch. physikal. Chem.*, 1909, **65**, 641). The solution round the cathode may thus become weaker, not only by the wandering away of complex anions containing copper, but by solvent molecules being transported into the cathodic compartment attached to the cation.

That such a transport of solvent molecules attached to ions may occur has been proved by Washburn (*Tech. Quart.*, 1908, **21**, No. 2), although in the cases studied the effect of hydration on migration ratios is not a marked one. Moreover, in their critical review of migration numbers, Noyes and Falk (*J. Amer. Chem. Soc.*, 1911, **33**, 1436) have shown that the true migration number is connected with the apparent or hydrated migration number by the equation

$$T^{Tr} = T + \Delta N_0 . N/N_0,$$

where ΔN_0 is the number of molecules of water transported to the cathode per faraday; N = number of equivalents of salt in solution associated with N_0 molecules of solvent; T = ordinary migration number (referred to solvent, which is assumed stationary); T^{Tr} = true migration number referred to a non-migrating substance.

If one accepts the hydration value obtained by Jones (*Carnegie Publ.*, No. 60, p. 85), this correction in concentrated solutions is of the order of 5—10 per cent., and therefore negligible in the light of the marked negative values obtained.

The effect of such a "hydration" effect will naturally be the more noticeable in concentrated solutions, but Bein's results (*Zeitsch. physikal. Chem.*, 1898, **27**, 50) for calcium chloride—a salt which, according to Abegg and Bodländer's complex theory (*Zeitsch. anorg. Chem.*, 1899, **20**, 453), should not form complex anions, and, according to Jones (*loc. cit.*), has a strongly hydrated cation—show how small this probable hydration effect is.

Chlorine, per cent.	Temperature.	n_{CaCl_2}
0·039	22°	0·447
0·42	24	0·405
0·99	21	0·390

Donnan and Bassett's theory postulates that the formation of the complex anion in solutions of copper and cobalt salts is attended by the absorption of heat, that is, it is favoured by a rise of temperature. Thus a solution of cobalt chloride in alcohol, which is blue at the ordinary temperature, becomes pinkish-red on cooling to −79°. If this is the case, an increase in temperature should bring about a decrease in the migration number due to the equilibrium

$$2Br' + xCuBr_2 \rightleftharpoons \left[\begin{matrix}(CuBr_2)_x \\ Br_2\end{matrix}\right]''$$

being driven to the right.

On the other hand, the effect of increasing temperature on a hydrated ion will be in all probability to cause a dissociation into a less hydrated or even an anhydrous ion (Lewis, *Zeitsch. physikal. Chem.*, 1905, **52**, 222; 1906, **56**, 223; Biltz, *loc. cit.*; Jones, *loc. cit.*). Jones and West have measured the temperature-coefficients of a large number of salts of varying degree of hydration, and they have concluded that:

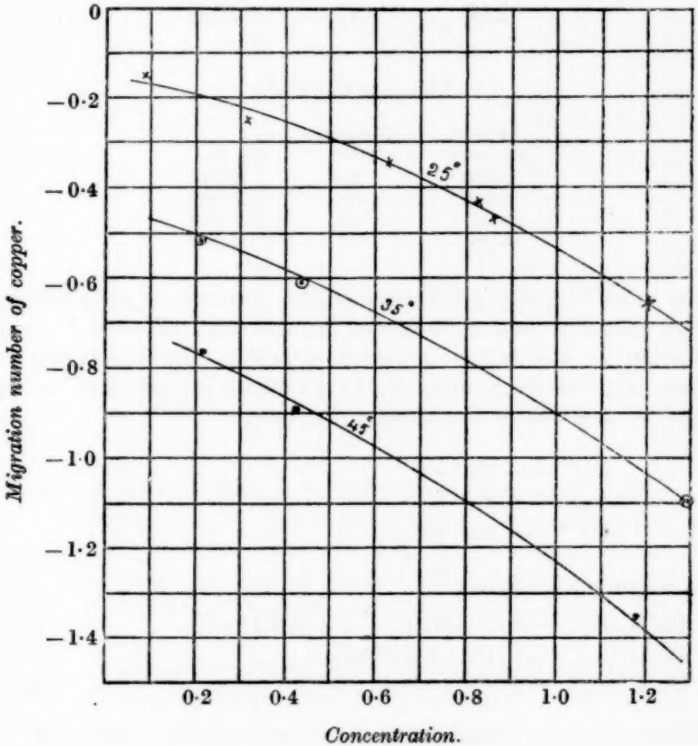
(1) The temperature-coefficients of aqueous solutions of electrolytes are greater the greater the hydrating power of the electrolyte.

(2) This large increase in conductivity with rise of temperature, in the case of salts forming hydrated ions, is due, in part, to the decreasing complexity of the hydrates formed around the ions.

Consequently, the equilibria

$$Cu(H_2O)_x^{\cdot\cdot} \rightleftharpoons Cu(H_2O)_{x-y}^{\cdot\cdot} + yH_2O \rightleftharpoons C\ u^{\cdot\cdot} + H_2O.$$

will be driven to the right, and abnormally low migration numbers must consequently tend to approach the normal value (0·4 approx.) with rise of temperature should the abnormality arise from a hydration effect.



In the diagram, the experimental results for copper bromide in alcohol are plotted as a typical example of the definite influence of temperature on the results.

These curves and the tables bring out clearly the rapid decrease in the migration number as the temperature of the solution rises in precise agreement with the demands of the complex theory, in direct contradiction to the demands of Jones' hydration theory.

Moreover, the following results of Bein for salt solutions, wherein

complex formation is scarcely to be expected, bear out the contention that the temperature has very slight influence on the cathodic migration number, even where the evidence of Jones and others indicates that such ions are more or less hydrated.

Calcium Chloride.

Chlorine, per cent.	Temperature.	u_{Ca}.
0·42	24°	0·405
0·42	97	0·426
0·77	20	0·395
0·85	94	0·451

Lithium Chloride.

Chlorine, per cent.	Temperature.	u_{Li}.
0·036	20°	0·371
0·036	97	0·389
0·20	25	0·324
0·20	97	0·381

The most convincing evidence of the presence of auto-complexes in the solutions under discussion is, however, afforded by a consideration of the cathodic copper deposit. In a solution of a copper salt, the mechanism of the electrode process may be represented by any one of the three equations:

$$Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot} + \odot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$Cu^{\cdot} \longrightarrow Cu + \odot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$Cu^{\cdot\cdot} \longrightarrow Cu + 2\odot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or, assuming hydration:

$$Cu(H_2O)_x^{\cdot\cdot} \longrightarrow Cu(H_2O)_y^{\cdot} + (x-y)H_2O + \odot \quad . \quad . \quad . \quad (1a)$$
$$Cu(H_2O)_y^{\cdot} \longrightarrow Cu + yH_2O + \odot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$
$$Cu(H_2O)_x^{\cdot\cdot} \longrightarrow Cu + xH_2O + 2\odot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

(see Foerster and Seidel, *Zeitsch. anorg. Chem.*, 1897, **14**, 106; Foerster and Coffetti, *Zeitsch. Elektrochem.*, 1904, **10**, 736; Bose, *ibid.*, 1898, **5**, 163; Heiberg, *ibid.*, 1903, **9**, 137; Abel, *ibid.*, 1903, **9**, 268; Bodländer and Storbeck, *Zeitsch. anorg. Chem.*, 1897, **14**, 106; Luther, *Zeitsch. physikal. Chem.*, 1900, **34**, 488; 1901, **36**, 385; Wohlwill, Borcher's "Elektrometallurgie," 3rd Ed., p. 198).

Should equation (3) or (3*a*) represent the cathode process, the ratio $\frac{\text{weight of copper deposited}}{\text{weight of silver in voltameter}} = 0{\cdot}295$, whilst any of the other equations would lead to the value 0·590. Table V shows how

much the experimental values differ from these. In this table, the last column gives the ratio $\frac{\text{weight of copper deposited}}{\text{weight of silver in voltameter}}$.

TABLE V.

Salt.	Solvent.	Temperature.	Concentration.	u_{Cu}.	$\frac{Cu}{Ag}$.
$CuBr_2$	water	35°	0·36	0·32	0·44
,,	,,	35	0·76	0·16	0·48
,,	,,	35	1·60	0·05	0·002
,,	,,	35	3·60	−0·35	0·000
,,	,,	45	0·36	0·19	0·44
,,	,,	45	1·60	−0·18	0·00
,,	,,	45	3·60	−0·88	0·000
$CuCl_2$	,,	35	0·25	0·34	0·324
,,	,,	35	0·75	0·24	0·308
,,	,,	35	2·00	0·181	0·090
,,	,,	35	4·00	−0·57	0·000
,,	,,	45	0·25	0·225	0·317
,,	,,	45	0·75	0·135	0·177
,,	,,	45	—	0·01	0·123
,,	,,	45	—	−0·4	0·000
$CuBr_2$	alcohol	35	0·21	−0·51	0·134
,,	,,	35	0·43	−0·60	0·115
,,	,,	35	1·30	−1·1	0·165
,,	,,	45	0·21	−0·77	0·095
,,	,,	45	0·43	−0·90	0·125
,,	,,	45	1·17	−1·35	0·219

These figures show that in dilute aqueous solutions much of the current is carried by the discharge of cupric to cuprous ions, and, indeed, actual observation showed that the deposits consisted of a heterogeneous mixture of copper and cuprous haloid salt. In such solutions, the electrode processes included in the equations (1) and (3), or, assuming hydration, (1*a*) and (3*a*), prevail, the cuprous ion being immediately precipitated as the insoluble chloride or bromide. The extent to which either process occurs has been shown by Seidel and others (*loc. cit.*) to depend on the variables, temperature, concentration, current density, and concentration of acid, and will in no way be influenced by the presence of hydrated ions in solution, whether those solutions are concentrated or dilute. In many of the more concentrated solutions, however, the ratio $\frac{Cu}{Ag}$ shows no quantitative agreement with Faraday's laws, whether the reduction to cuprous ion or to copper itself occurs, or both. In a number of experiments, the ratio $\frac{Cu}{Ag}$ falls to zero, that is, no

copper or cuprous salt whatsoever is deposited on the cathode. This abnormality, incapable of explanation as it is by the hydration theory, may be satisfactorily explained by the theory of auto-complexes. In concentrated solutions, such equilibria as

$$Cu^{\cdot\cdot} + x CuBr_2 + 2Br' \rightleftharpoons Cu^{\cdot\cdot} + \left[\begin{matrix}(CuBr_2)_x \\ Br_2\end{matrix}\right]''$$

are postulated, the undissociated salt, of relatively weak electro-affinity, being forced into a complex anion. As the cuprous ion, however, possesses a more noble potential than does the cupric ion, that is, have a weaker electroaffinity, the cuprous salts, according to Abegg and Bodländer's complex theory (*loc. cit.*), will be more readily forced into a complex than the corresponding cupric salts (Donnan, Abegg's "Handbuch," Kupfer, p. 517). In concentrated solutions, seeing that no metallic copper or copper salt is precipitated on the cathode, the current must be wholly carried in the following way:

$$Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot} + \odot$$

(possibly $Cu(H_2O)_x^{\cdot\cdot} \longrightarrow Cu(H_2O)_y^{\cdot\cdot} + (x-y)H_2O + \odot$); the cuprous salt, however, instead of being thrown out of solution, as happens in the more dilute solution, and as demanded by the hydration theory, forms a soluble cupri-cupro-salt with the cupric salt already in solution. It is precisely in those solutions where the absence of deposit on the cathode occurs, that the migration number is so strongly negative. The soluble nature of this cupri-cupro-salt, coupled with the markedly negative migration number, points very strongly to the assumption that such a reaction as the following occurs:

$$Cu^{\cdot\cdot} + 2Br' + x CuBr \rightleftharpoons Cu^{\cdot\cdot} + \left[\begin{matrix}(CuBr_2)_x \\ Br_2\end{matrix}\right]''.$$

In further confirmation of the views here put forward, a migration experiment was carried out in a U-tube, first with $4N$-cupric chloride, and secondly with $4N$-cupric chloride which had been warmed with cuprous chloride, these lower layers being covered by $N/10$-cupric chloride. In both cases, the brown boundary moved towards the anode.

Summary.

(1) The effect of temperature and concentration on the migration number of solutions (aqueous and alcoholic) of copper bromide and chloride has been investigated.

(2) The effect of increasing temperature and concentration is to cause a marked drop in the migration number of the copper ion, which in concentrated solutions approaches -1 in value.

(3) The formation in concentrated solutions of soluble cupri-cupro-haloid salts at the electrode of the migration vessel has been proved.

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CXIX.—*Colloidal Electrolytes: Soap Solutions as a Type.*

By JAMES WILLIAM MCBAIN, MARY EVELYN LAING, and ALAN FRANCIS TITLEY.

BASED on the extensive data obtained from the study of soap solutions in this laboratory since 1908, McBain and Salmon have defined a new class of compounds, colloidal electrolytes, to which a very large number of substances of great industrial importance may be expected to belong. This comprehensive group is defined as comprising salts in which one ion has been replaced by an ionic micelle of high valency, mobility, conductivity, and degree of solvation. Regarded from another point of view, this means that any colloid which carries electrical charges will in some measure approach the behaviour of a typical colloidal electrolyte. Light is also shed on the properties of colloidal solutions which contain acids, bases, or salts, or to which these have been added. The consistent application of this point of view leads to an ionic micelle theory of all charged colloids; the current assumption that the other charge is carried by the solvent is replaced by the hypothesis that free ions of charge equal and opposite to that of the charged colloid are present in the sol or gel.

Soap was chosen as the subject for investigation, not only because of its industrial importance, but because of its known and definite chemical simplicity and constitution as compared with dyes or protein derivatives, etc. Furthermore, chemical literature contained apparently irreconcilable data obtained by a number of well-known authorities, such as Krafft, Smits, and Kahlenberg. These either assumed that soap was an ordinary neutral colloid, or else, on the contrary, an electrolyte which had suffered extreme hydrolysis with the formation of colloidal residue suspended in a strongly alkaline solution. Each investigator, moreover, considered that the whole problem was solved.

Now it is demonstrated through the measurements of con-

ductivity, osmotic activity, and alkalinity of soap solutions communicated from this laboratory that in concentrated solution the soaps are typical colloidal electrolytes. On dilution, they gradually break down into simple salts. In extreme dilution, acid soaps separate out through hydrolysis. Both catalytic and electromotive force measurements have shown that, except in extreme dilution, hydrolysis is a very minor consideration, the hydroxyl ion being present to the extent of only about $N/1000$.

The argument for the existence of the ionic micelle was as follows: In all concentrations the conductivity is high and the osmotic activity, which was measured by the unexceptionable method of dew-point lowering, is only moderate. Hence, in concentrated soap solutions, even if all the osmotic activity is earmarked for the potassium, sodium, or ammonium ion, nearly or quite half of the conductivity remains to be accounted for. This conductivity must evidently be ascribed to some constituent that does not exert appreciable osmotic pressure and that therefore must be colloidal. One of us (J.W.M., *Trans. Faraday Soc.*, 1913, **9**, 99; *Kolloid Zeitsch.*, 1913, **12**, 256) has shown how this is possible and probable by applying the principle of Stokes's law to the hypothesis of a heavily charged, heavily hydrated ionic micelle which would exhibit excellent conductivity and high viscosity at the same time.

Although our investigation of soap solutions has only reached its first stage, it has been possible on the basis of the above reasoning to set up a comprehensive theory which explains and reconciles all the mass of data of the most diverse sort which has already been accumulated. The various details of this theory, beyond the rough outline given above, will be mentioned and discussed in turn as we come to the new and confirmatory experimental evidence described below.

This communication presents measurements of the freezing point and conductivity of nearly all the soap solutions which can be studied at 0°. Such comprise solutions of the potassium salts of the saturated fatty acids up to and including the laurate (C_{12}) in all concentrations, and of the sodium salts up to the octoate (C_8). Further, the values for potassium oleate can be measured up to $0{\cdot}6N$ ($0{\cdot}8N$ is a solid jelly at the ordinary temperature), and sodium oleate up to $0{\cdot}4N$, a solution which is already quite viscous.* All other sodium, potassium, and ammonium soaps

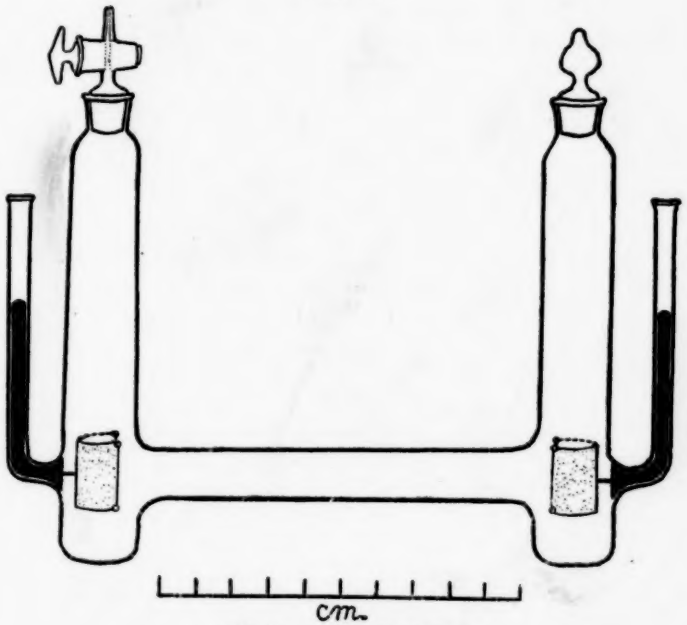
* The stable form of the sodium oleate solutions at 18° is a white curd. The conductivity at 18° of a very slightly alkaline $0{\cdot}4N_w$ sodium oleate solution which has solidified to a stiff white curd is still 95 per cent. as great as when it is a clear oily liquid at the same temperature.—M. E. L.

gelatinise, crystallise, sediment, or solidify at temperatures between 10° and 90°, as the case may be. Even potassium laurate and decoate usually separate out at above 0°. This is another reason why our chief experimental work hitherto has had to be carried out at 90°, in spite of the greatly increased difficulties entailed.

The Conductivity of Soap Solutions at 18°.*

In all our experiments, the precautions described in previous communications were observed. All instruments and vessels were

FIG. 1.



Cell for good conductors.

standardised. The soaps were likewise prepared from potassium drippings and fatty acids by methods previously described. Concentrations are expressed in weight normality, N_w (mols. per 1000 grams of water), and in volume normality, N_v, the latter referring only to the temperature of the particular experiment.

The conductivity measurements of solutions from $N/10$ upwards were carried out in a simple and convenient cell of Jena glass of the form shown in Fig. 1, specially designed for excellent conductors. The large platinum electrodes were coated with grey

* Experiments by M. E. L.

platinum sponge, and they were held firmly in position by glass rods fused to the cell wall and to each corner of the platinum. The cell constant was 13·20. The conductivity water possessed a specific conductivity of $1-2\times10^{-6}$, for which no correction was made. Solutions from $N/10$ downwards were studied in the borosilicate cell described by one of us (M.E.L., T., 1918, **113**, 245). The two cells gave identical values for the $N/10$-solutions.

The results are recorded in tables I—IV. The first column gives the weight normality, N_w, of the soap; the second, the volume normality at 18°, N_v; the third, the values obtained for the specific conductivity, κ, the values given being the final results from wholly independent solutions; * the fourth,† the density, D_4^{18}; the fifth, the equivalent conductivity, Λ; the last column, the apparent degree of dissociation, α, where $\alpha=\mu_v/\mu_\infty$, μ_∞ being taken as equal to 85·4 for potassium salts, except the *n*-octoate (88·2) and sodium oleate (64·3).

TABLE I.

Conductivity of Potassium Laurate at 18·00°.

N_w.	N_v.	κ.	Λ.	α.
2·000	1·378	0·05947	43·14	0·505
1·500	1·118	0·05131	45·80	0·536
1·000	0·820	0·03824 0·03889 0·03866	47·09	0·551
0·750	0·641	0·03032	47·21	0·553
0·500	0·449	0·02042	45·44	0·532
0·400	0·367	0·01622	44·22	0·518
0·200	0·191	0·007984 0·007984	41·77	0·489
0·100	0·098	0·004322 0·004299	44·03	0·516
0·050	0·049	0·002713	54·89	0·643
0·0247	0·024	0·001702	68·74	0·805
0·010	0·010	0·0007539	75·44	0·883

TABLE II.

Conductivity of Potassium Oleate at 18·00°.

N_w.	N_v.	κ.	D_4^{18}.	Λ.	α.
0·600	0·540	0·02023 0·02013	1·0070	37·25	0·436
0·400	0·363	0·01304	1·0030	36·72	0·430
0·200	0·188	0·006248	0·9999	33·30	0·390
0·100	0·097	0·002877	0·9996	29·74	0·348
0·050	0·049	0·001451	0·9991	29·57	0·346
$N/32$	0·031	0·001035	0·9989	33·32	0·390
0·010	0·008	0·0004198	0·9987	51·95	0·608

* One preparation of oleic acid gave quite colourless clear soap solutions, the other pale yellow solutions.

† Omitted in Tables I and IV, as new determinations were not required.

TABLE III.

Conductivity of Sodium Oleate at 18·00°.

N_w.	N_v.	κ.	D_4^{18}.	Λ.	α.
0·600	0·510	0·01104	1·0050	21·67	0·337
0·400	0·357	{0·007362 / 0·007476}	1·0020	20·80	0·323
0·200	0·197	{0·003994 / 0·003855}	0·9997	19·77	0·307
0·100	0·099	0·001922	0·9993	20·46	0·318
0·050	0·049	0·0009966	0·9987	20·59	0·320
0·010	0·010	0·0002956	0·9986	30·09	0·468

TABLE IV.

Conductivity of Potassium n-*Octoate at* 18·00°.

N_w.	N_v.	κ.	Λ.	α.
2·000	1·601	0·06757	42·24	0·479
1·000	0·895	0·04208	48·60	0·551
0·750	0·690	0·03345	49·75	0·564
0·500	0·472	0·02455	53·00	0·601
0·200	0·198	0·01185	63·05	0·715
0·100	0·099	0·006456	69·50	0·788

The density in every case is very slightly greater than that of water, as is always observed for potassium and sodium salts of the lower fatty acids.

Some of these solutions have been measured at neighbouring temperatures by other investigators with fewer experimental precautions (Kahlenberg and Schreiner, *Zeitsch. physikal. Chem.*, 1898, **27**, 552; Dennhardt, *Diss.*, 1898; *Ann. Phys. Chem.*, 1899, [iii], **67**, 325; Kurtzmann, *Diss.*, 1914; *Koll. Chem. Beihefte*, 1914, **5**, 465; Reychler, Eighth International Congress of Applied Chemistry). Their results differ more or less irregularly from ours by amounts varying from 0 to 30 per cent. in both directions. The smaller differences are chiefly attributable to alkali dissolved from the glass, an important source of error in the study of soap solutions (see McBain and Taylor, *loc. cit.*, on whose exact study the validity of these experiments is based). On the whole, the agreement is substantial, and our results are probably accurate to about 1 per cent., with the possible exception of sodium oleate.

The effect of time is of the order of magnitude of 1 per cent., but all our solutions were kept for several days at the ordinary temperature to allow them to become quite constant before being measured. The data refer to clear solutions in every case, except $N/20$-potassium laurate, which is always cloudy. Thus many of these solutions are supersaturated or metastable with respect to

the separation of indefinite acid soaps. The latter dissolve on warming, and the metastable solutions can then be preserved for long periods.

The Explanation of the Good Conductivity of these Colloidal Electrolytes, together with their Anomalous Maxima and Minima, by Means of the Hypothesis of the Ionic Micelle.

It will be recollected that hydrolysis has been shown to occur to only a slight extent in concentrated solutions of soap, so that in any case it cannot be adduced to explain an appreciable part of the good conductivity exhibited by soaps (and by hexadecanesulphonic acid and its salts). This must find another explanation.

The conductivity results are best discussed by showing them in the form of a graph for comparison. This is done in Fig. 2, where the equivalent conductivities are plotted as ordinates against the concentration, N_v, as abscissæ. The figure also includes curves for the results of the higher potassium soaps at 90°.

The most striking point about these curves is that they represent moderately good conductivities even in concentrated solutions. Indeed, in many cases the conductivity curve, after passing through a minimum, rises on further concentration to a maximum, a phenomenon otherwise unknown in any aqueous solution,* except for Reychler's hexadecanesulphonic acid, which is also a soap (*Bull. Soc. chim. Belg.*, 1913, **27**, 113). This effect is more pronounced at 18° than at 90°. Again, for any one saturated fatty acid, the potassium salt exhibits this behaviour to a distinctly greater degree than does the corresponding sodium soap. The oleates differ entirely from the soaps of the saturated fatty acids in that sodium oleate is a very much more typical soap in this respect.

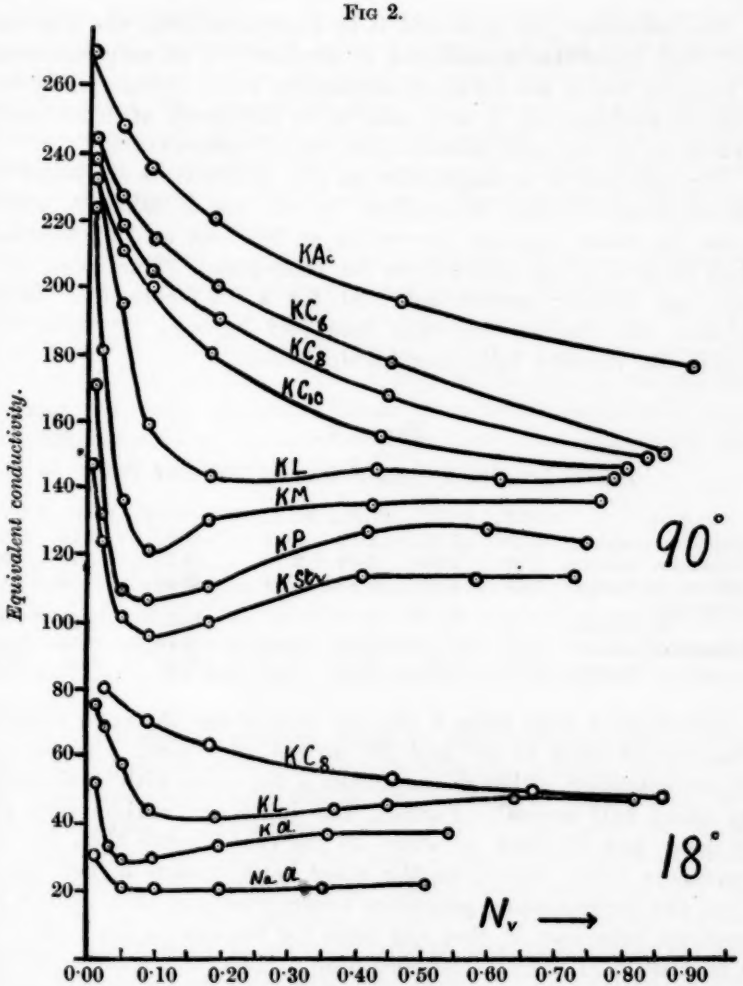
The existence of the minimum as an experimental fact has shown that on further increase of concentration the changes effected are such as to increase the conductivity. This cannot possibly be due to dissociation suddenly increasing again for a limited interval, nor can it be due to free hydroxyl ions, since the latter factor is negligibly small.

The increase of conductivity with increase of concentration must therefore be due to the replacement of the simple laurate anion by an ionic micelle of higher mobility. Thus the effect of decreasing dissociation is more than counterbalanced by this replacement. Finally, however, a maximum is reached where the steadily

* Sloan (*J. Amer. Chem. Soc.*, 1910, **32**, 946) finds that at 0° the equivalent conductivity of aqueous potassium iodide is constant over a considerable range of concentration.

diminishing dissociation of the colloidal electrolyte itself overbalances all other factors. That the conductivity of the ionic micelle is greatest in concentrated solutions, where its hydration is least, will be discussed below.

FIG 2.



Equivalent conductivity of soap solutions at 18° and at 90°.

The position of the minimum at the ordinary temperature is still only at $N/5$, but the greater formation of ionic micelle is evinced by the quite slow rise of the curve on dilution at the solution $N/10$ as contrasted with its rapid rise at 90°. This behaviour was predicted by McBain and Salmon, as was also the fact that

the minimum for potassium oleate occurs between $N/10$ and $N/20$ owing to the greater tendency of this higher soap to form micelle.

The Temperature-coefficient of Conductivity of Solutions.

The behaviour just described is in accordance with the abnormally high temperature-coefficient of conductivity in soap solutions, a property which was formerly ascribed to rapid increase of hydrolysis on heating, but is now seen to be the result of diminishing hydration of the ionic micelle with rise of temperature.

The influence of concentration on the temperature-coefficient of the conductivity may be analysed by the use of table V, which gives the ratios between the values at 90° and at 18°, together with those of a few electrolytes for comparison. Kurzmann (*loc. cit.*) has already pointed out that for a 0·6N-potassium oleate solution the conductivity rises three-fold between 20° and 90°, whilst the viscosity falls four hundred-fold.

TABLE V.

Ratios between Conductivities at 90° *and* 18°.

Salt.	0·01N_{v}.	0·05N_{v}.	0·1N_{v}.	0·2N_{v}.	0·5—0·6N_{v}.	1·0N_{v}.	2·0N_{v}.
Sodium acetate ...	3·25	3·22	3·19	3·13	3·12	3·14	3·33
Potassium acetate	2·88	2·85	2·82	2·79	2·75	2·79	2·98
Sodium hydroxide	2·53	2·46	2·46	2·44	2·45	2·50	—
Potassium hydroxide	—	—	—	—	—	2·22	—
Potassium octoate.	—	—	2·95	3·03	3·18	3·06	—
„ laurate	3·09	3·56	3·62	3·45	3·22	3·04	2·86

It is evident from table V that for electrolytes the ratio between the conductivities at 90° and 20° do not vary much with change of concentration, although they make a flat curve with a minimum at about half normal. Further, the values for sodium salts are in every case 0·3 unit, or about 10 per cent. higher than for the potassium salts. Soaps, on the other hand, possess higher values than the corresponding potassium electrolytes, and they exhibit an opposite behaviour in that the ratio for the temperature effect is a maximum in medium concentration. Kurzmann's ratios, as far as they go, appear to parallel ours, but are 0·3 to 0·4 unit lower.

The customary temperature-coefficients of conductivity involve three separate factors for any electrolyte and five for a colloidal electrolyte. The first two are the specific mobilities of the two ions, of which those with lowest mobility have the highest temperature-coefficient, the third is the change of dissociation with temperature, whilst in the case of a colloidal electrolyte there is

the further factor of the change in equilibrium between ions and ionic micelle in addition to the temperature-coefficient of the latter itself. The more exact analysis is simple for electrolytes, but must remain in abeyance for the soaps until we have obtained the further experimental data contemplated. The higher temperature-coefficient for sodium ion is in accordance with the recognised probability of its hydration being greater than that of potassium, and that the same factor of hydration would explain the data for soap solutions. The increase of colloid with lowering of temperature is also a factor which might conceivably operate in either direction according as to whether this is increase of highly mobile ionic micelle or increase of neutral colloid at the expense of electrolyte and micelle.

The other case of a colloidal electrolyte exhibiting an anomalous conductivity curve is hexadecylsulphonic acid (Reychler, *loc. cit.*), which exhibits a minimum conductivity of 135 mhos. (to 149 mhos.) in $N/30$-solution at 56° (or 55°), but it has been measured only up to $N/15$-solution. Indeed, it is tantalising in the extreme to note how many promising cases of colloidal electrolytes have been studied only in dilute solution, probably the reason why this type of behaviour has not been long familiar.

The Osmotic and Freezing-point Methods.

These data are not nearly so accessible as one might expect for the case of colloidal electrolytes in which we are interested, as a brief examination will show. Indeed, the data of McBain and Salmon constitute the only satisfactory determinations hitherto recorded.

The freezing-point method, which is the subject of our present study, is the osmotic method *par excellence* where it can be applied, but it is here surprisingly limited in its range of application. Its trustworthiness is undisputed, and, further, it may be made accurate. The boiling-point method is wholly untrustworthy in its application to solutions that froth and contain colloids on account of the effects of enclosed air, which, as McBain and Taylor proved experimentally, entirely vitiate the indications of the method, and may lead to large apparent lowering instead of rise of boiling point. The vapour-pressure method, even in the hands of Smits, led to equally erroneous results on account of the same unsuspected error. McBain and Taylor found that weeks of effort were required to obtain a single rather inexact measurement. Osmometer data, again, depend so much on the mode of interpretation that it is inadvisable to build upon such a foundation.

The lowering of dew-point method has been developed by McBain and Salmon, and measurements have been made of nearly a hundred soap solutions. It possessed the double advantage that it could be used at various temperatures, and that the presence of air had no influence on the results. It is, however, an unfamiliar method which has not been previously applied to the study of solutions.

The existing literature consists of two measurements by Kahlenberg and Schreiner of the lowering of freezing point of $N/8$- and $N/16$-sodium oleate, and the dew-point data of McBain and Salmon, mostly referring to a temperature of 90°. The freezing-point measurements here presented were carried out in order to study the effect of temperature and obtain further corroborative evidence by this independent method.

The great difficulty is to measure the soaps while in the form of homogeneous solution. On cooling in the freezing apparatus, they usually become turbid, with the formation of fine, white or colourless, crystalline flakes, presumably of somewhat acid soap. This may often be avoided, and the soaps can be measured in the metastable condition. It should be noted that they are only a few degrees below the temperature at which the homogeneous form of the system constitutes stable reversible equilibrium. Indeed, perhaps the most important fact for the whole study of soap solutions is that the solutions constitute perfect reversible equilibria in which colloid, micelle, and crystalloid alike participate (see McBain and Taylor, *loc. cit.*). Incidentally, this would lead us to infer that colloidal systems in general represent the equilibria much more often than is usually recognised, owing to the conditions not being kept constant.

Two methods were used, namely, the ordinary one of Beckmann and that of Richards (*Zeitsch. physikal. Chem.*, 1903, **44**, 563; *J. Amer. Chem. Soc.*, 1903, **25**, 291). The latter is the quickest, and probably also the most accurate, of the precision methods, and it had been shown to be capable of yielding results accurate to about 0·0003°. It consists of the use of a Dewar vacuum vessel surrounded by a bath of the freezing temperature, and containing a solution which is full of finely powdered pure ice. When, after stirring, equilibria is attained, a portion of the solution is withdrawn for analysis. For the latter we used either a Zeiss interferometer in conjunction with a graph prepared from standard solutions, or else we evaporated the solutions to dryness and weighed the residue. The former method, for example, is suitable for potassium acetate, the latter for potassium laurate. Although our object was not great accuracy, but chiefly trustworthiness and

results free from distortion, we used a standard thermometer graduated in five-hundredths of a degree, the scale and readings of which were corrected to the readings on the international hydrogen thermometer at the Reichsanstalt in 1913, and this thermometer was kept permanently at 0°.

Results by the ordinary Beckmann method are usually much distorted by the effect of the low convergence temperature, which makes the lowering too great. In concentrated solutions, moreover, the alteration of concentration due to undercooling is very appreciable, and tends in the same direction. This error cannot readily be allowed for by the ordinary method of calculation in the case of soap solutions, although it is very marked, probably on account of the protective action of the colloid on incipient ice crystals. Thus, unless an inoculating rod was used, the undercooling easily exceeded 7° for an hour at a time, in spite of vigorous stirring. Great care was taken to minimise undercooling and to raise the convergence temperature. The important point to remember in what followed is that the lowering observed is never less than the true value, but that, on the contrary, the osmotic effect is exaggerated.

The Freezing-point Data.

Table VI presents the results of the Beckmann freezing method. The results marked with an asterisk denote turbid solutions. The potassium myristate (C_{14}) separated out completely on cooling with marked evolution of heat; the liquid froze a few thousandths of a degree below 0°.

TABLE VI.*

Lowering of Freezing Point by Beckmann Method.

	$0{\cdot}2N_w$.	$0{\cdot}5N_w$.	$1{\cdot}0N_w$.	$2{\cdot}0N_w$.
Potassium acetate.....	0·749°	1·948°	3·82°	8·56°
Sodium acetate	0·704	1·774	3·739	8·10
Potassium *n*-octoate...	0·742	1·860	2·519	3·146
,, decoate...	0·649	0·752	1·014	—
,, laurate ...	0·197 0·245	0·332 0·371	0·623 0·737	0·355 1·460

Also 0·75 sodium acetate, 2·740°; 1·5 sodium acetate, 5·83°; 0·05 potassium laurate, 0·177°; 0·1 potassium laurate, 0·212°; 1·0 sodium *n*-octoate, 2·445°; 0·6 potassium oleate, 0·348°; 0·4 potassium oleate, 0·215°; 0·4 sodium oleate, 0·146°; 0·2 sodium oleate, 0·095°; 3·0 potassium *n*-octoate, 4·71°.

* Experiments by M. E. L. or J. W. M.

Table VII contains the results of the Richards method, in which it is a matter of great difficulty to avoid separation of soap with resulting turbidity. Here again such solutions are designated by an asterisk. Many unsuccessful attempts were made to measure clear laurate solutions until, finally, in one case a solution which had been carefully frozen without becoming turbid was introduced in this form and stirred very slowly until the temperature was constant; the liquid then withdrawn was clear.

TABLE VII.*

Lowering of Freezing Point (corr.) by Richards' Method.

Potassium acetate.		Potassium acetate.		Potassium oleate.		Potassium laurate.	
$0{\cdot}824N_w$	2·934°	$0{\cdot}323N_w$	1·120°	$1{\cdot}196N_w$	0·117°	$0{\cdot}684N_w$	0·381°
0·718	2·522	0·316	1·102	0·095	0·088	0·569	0·337
0·538	1·890	0·292	1·007	0·065	0·064	0·491	0·304
0·529	1·830	0·258	0·882	Potassium		0·175	0·182
0·488	1·712	0·234	0·800	*n*-octoate		0·124	0·168
0·469	1·635	0·206	0·690			0·0829	0·154
0·425	1·490	0·169	0·588	$0{\cdot}811N_w$	2·367	0·0361	0·120
0·378	1·324	0·146	0·507	0·509	1·912	0·456	0·328
0·352	1·230	0·113	0·404	0·405	1·534	0·262	0·242
—	—	—	—	0·269	1·004	0·121	0·203
—	—	—	—	0·169	0·610	0·093	0·164

The values obtained by the Beckmann method are in many cases higher than the more accurate data of table VII. Further, the data for solutions which have become turbid through separation of solid are distinctly less than those for clear solutions.

The lowering of freezing point indicates the total concentration of crystalloid. This is shown in table VIII for round concentrations, in most cases making use of the data of table VII in preference to those of table VI, and, of course, taking only the data for clear solutions. The numbers are obtained by dividing the lowerings by 1·858, the cryoscopic constant for water.

TABLE VIII.

Total Concentration of Crystalloid in these Solutions.

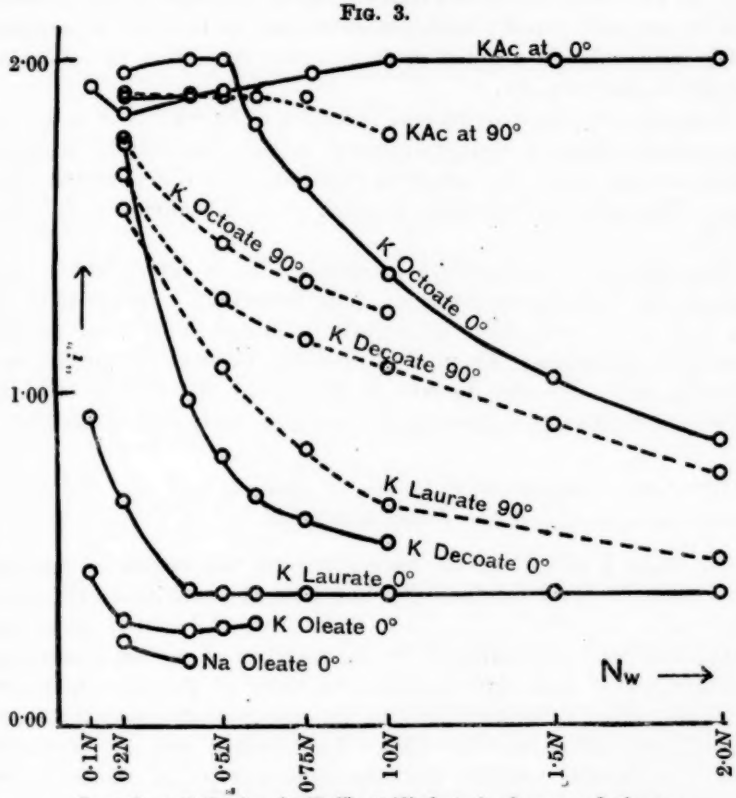
	$0{\cdot}1N_w$.	$0{\cdot}2N_w$.	$0{\cdot}4N_w$.	$0{\cdot}5N_w$.	$0{\cdot}6N_w$.	$1{\cdot}0N_w$.	$2{\cdot}0N_w$
Potassium acetate.....	0·19	0·37	0·76	0·94	1·13	2·03	4·60
Sodium acetate	—	0·38	0·76	0·95	1·16	2·01	4·36
Potassium octoate ...	—	0·37	0·81	1·00	1·13	1·36	1·693
„ decoate ...	—	0·35	0·39	0·40	0·41	0·55	—
„ laurate ...	0·093	0·136	0·164	0·20	0·24	0·40	0·79
„ oleate	0·046	0·064	0·116	0·15	0·19	—	—
Sodium oleate	—	0·051	0·079	—	—	—	—

* Experiments by A. F. T.

Also sodium octoate, $1{\cdot}0N_w$, 1·32; potassium octoate, $3{\cdot}0N_w$, 2·53.

The lowering of freezing point is so large as to be indisputable, although it is in many of the solutions less than for an electrolyte of the same concentration.

FIG. 3.



Osmotic activity (van't Hoff's "i" factor) of soap solutions at 0° and at 90°.

The Effect of Temperature on the Osmotic Activity of Soaps.

The significance of these results is more apparent from a study of the results plotted graphically, as in Fig. 3, in the form of the value of the van't Hoff factor "*i*." This is merely the ratio between the actual lowering and that predicted theoretically for a perfect non-electrolyte of the same concentration, namely, 1·858° per equivalent of normality. In Fig. 3 the values of "*i*" are plotted against total weight normality of the solution. Some of the values at 90° are included for comparison.

First, with regard to the absolute magnitude of the osmotic effect in concentration of the higher soaps above $N/3$, it lies between 1/5 and 2/5 of that for a crystalloid such as sucrose, or between 1/10 and 2/10 of that for an acetate. Further, the osmotic effect tends to be constant for concentrated solutions. At 90°, on the other hand, the osmotic effect is several times greater, and it decreases rapidly with concentration up to $1{\cdot}5N$ or beyond. Both facts indicate a much more complete formation of colloid at the lower temperature.

Secondly, the familiar general influence of hydration in magnifying osmotic effects is clearly apparent in the data for the acetates, which in turn stimulate complete dissociation in concentrated solution. The effect of hydration is much more in evidence at 0° than at 90°.

The octoate is particularly interesting in its intermediate position in the homologous series as in its behaviour. In solutions up to $N/2$, it is quite like the acetate, although with even greater apparent hydration. From $N/2$ upwards, however, it rapidly and steadily falls, like the decoate at 90°, until the osmotic activity is only 0·85 that of a theoretical (non-hydrated) non-electrolyte.

The Concentration of Potassion or Sodion, and the Mobility of the Ionic Micelle at 18°.

In tables I to IV, values were given for the degree of dissociation deduced from conductivity based on the mobilities $K^{\cdot}=64{\cdot}7$, $Na^{\cdot}=43{\cdot}6$, $C_2'=34{\cdot}7$, $C_8'=23{\cdot}5$, $C_{12}'=20{\cdot}7$, $C_{18}'=20{\cdot}7$, where the fatty acid ions are indicated by the number of carbon atoms they contain. Our data, supplemented by those of Kohlrausch for the acetates, when calculated lead to the provisional concentration of alkali ions given in table IX*a*. This tacitly assumes that even the ionic micelle exhibits the same conductivity as the ions from which it originates. An alternative basis of calculation is contained in table IX*b*, to be explained below.

TABLE IX.

Concentration of Potassion or Sodion at 18°.

(a) *Assuming Ordinary Ionic Mobilities.*

Substance.	0·1*N*.	0·2*N*.	0·4*N*.	0·5*N*.	0·6*N*.	1·0*N*.	2·0*N*.
Potassium acetate.....	0·084	0·159	0·298	0·360	0·422	0·634	1·002
Sodium acetate	0·069	0·129	0·235	0·278	0·324	0·467	0·680
Potassium octoate ...	0·079	0·143	0·251	0·300	0·350	0·551	0·958
„ laurate ...	0·052	0·098	0·207	0·265	0·324	0·551	1·01
„ oleate	0·035	0·078	0·172	0·217	0·262	—	—
Sodium oleate	0·032	0·061	0·129	0·165	0·192	—	—

TABLE IX. (*continued*).

(b) *If Ionic Micelle has the same Mobility as Potassion.*

Substance.	0·1*N*.	0·2*N*.	0·4*N*.	0·5*N*.	0·6*N*.	1·0*N*	2·0*N*.
Potassium octoate ...	0·079	0·143	0·251	0·300	0·342	0·504	0·822
,, laurate ...	0·034	0·065	0·137	0·176	0·214	0·36	0·66
,, oleate	0·023	0·051	0·114	0·143	0·173	—	—
Sodium oleate	0·019	0·037	0·077	0·098	0·120	—	—

Taking, first, the tentative results of table IX*a* for the oleates and laurate, and comparing them with the data of table VIII, it is at once apparent that the supposed concentration of potassion or sodion greatly exceeds the total concentration of crystalloidal matter present, except for the most dilute solutions. Thus, for 0·4*N*-solutions, the discrepancies amount to about 0·05*N*.

We are forced to revise the assumption made with regard to the conductivity of the ionic micelle, and to ascribe to it a conductivity equal to that of the potassion if conductivity and osmotic measurements are to be harmonised at all. In table IX*b*, then, the conductivity data are calculated on the assumption that the ionic micelle has an equivalent conductivity of 64·7, which is more than three times as great as that of the true oleate or oleate ion. This is, however, in agreement with the theoretical considerations advanced by one of us (J.W.M., *Trans. Faraday Soc.*, 1913, **9**, 99; *Kolloid Zeitsch.*, 1913, **13**, 56), and already applied by one of us in a previous communication with Salmon (*loc. cit.*). It was found necessary to make a similar assumption in the case of concentrated solutions at 90°.

Once again it is necessary to recall that the known sources of distortion of the experimental data operate in such direction as to emphasise the argument on which our conclusions are based. Thus, owing presumably to hydration, osmotic data in general are obviously magnified (see, for example, Landolt-Börnstein "Tabellen," where apparent dissociation frequently exceeds 100 per cent.). Again, high viscosity is conceded to have the effect of diminishing apparent conductivity. Yet, in spite of this, the outstanding experimental result is that in soap solutions the osmotic effect is only sufficient to explain about half of the conductivity exhibited.

The effects just discussed for the case of ordinary electrolytes are exemplified in the usual unmistakable fashion by the results for the acetates and the more dilute solutions of the octoate. In these cases, the osmotic activity as measured considerably exceeds the total predicted from conductivity. In the more concentrated solutions of octoate, however, the soap character predominates

sufficiently to mask this, and they show more than 50 per cent. of colloid (see below, table X).

In this intermediate case of potassium octoate in table IX*b* use was made of Fig. 3 in computing the average mobilities of the varying mixtures of ions and ionic micelle here present. For solutions between 0·5 and 2·0*N*, it was simply assumed that Λ_∞ varied linearly with the i value from 88·2 for $i=2·00$ to 108·3 for $i=0·40$. This is a first approximation pending the results of actual measurements of migration now being carried out with soap solutions.

The Amounts of Crystalloid and Colloid in Soap Solutions.

The total amounts of crystalloidal matter other than potassion or sodion are obtained by subtracting the numbers in table IX*b* for sodium or potassium from those of table VIII for total crystalloids; the results are given in table X. Further, these amounts subtracted from the total concentration leave the amounts which it is necessary to regard as colloid. Further, since the total amount of, say, oleate present must be the sum of crystalloidal and colloidal oleate, the amount of colloid is simply the total concentration less the value for crystalloid given in table X. These values are collected in table XI, and the latter includes for comparison a few results found by the dew-point method at 90°.

TABLE X.

Crystalloidal Matter other than Potassion or Sodion.

Substance.	0·1*N*.	0·2*N*.	0·4*N*.	0·5*N*.	0·6*N*.	1·0*N*.	2·0*N*.
Potassium acetate.....	0·106	0·211	0·462	0·580	0·708	1·396	3·598
Sodium acetate	—	0·251	0·525	0·672	0·836	1·543	3·680
Potassium octoate ...	—	0·248	0·559	0·700	0·790	0·856	0·868
,, laurate ...	0·059	0·071	0·027	0·02	0·03	0·04	0·13
,, oleate	0·023	0·013	0·002	0·007	0·014	—	—
Sodium oleate	—	0·014	0·002	—	—	—	—

TABLE XI.

Total Concentration of Colloid.

Substance.	0·1*N*.	0·2*N*.	0·4*N*.	0·5*N*.	0·6*N*.	1·0*N*.	2·0*N*.
Potassium octoate	—	−0·05	−0·06	−0·2	−0·19	+0·144	+1·132
Do. at 90°	—	−0·02	—	+0·07	—	+0·28	—
Potassium laurate	0·041	0·129	0·373	0·48	0·57	0·96	1·87
Do. at 90°	—	−0·01	—	+0·22	—	+0·85	+1·89
Potassium oleate...	0·077	0·187	0·398	0·493	0·586	—	—
Sodium oleate	—	0·186	0·398	—	—	—	—

The results given in tables X and XI may be summarised in the statement that in all but the most dilute solutions of the laurate, and still more so with the oleates, the soap exists almost entirely as colloid. The 0·1*N*- and 0·2*N*-laurate, and the 2·0*N*-octoate, contain comparable amounts each of crystalloid and colloid.

It is instructive to note that the effects of hydration are much less evident at 90°, which agrees well with the extensive investigations of H. C. Jones and others on the solvate theory. The results with soap solutions in general afford strong support for a solvate form of the dissociation theory. For instance, the change in hydration with temperature explains the very high temperature-coefficient of the conductivity of soap solution.

The second effect of temperature is that much more colloid is formed at lower temperatures. This is very evident in the case of the higher soaps. At 90°, as at the ordinary temperature, very dilute solutions of soap contain but little colloid, and the soap is essentially in the form of a simple electrolyte. At the lower temperature, however, the formation of colloid sets in at much lower concentration.

The combined influences just referred to are most apparent in the intermediate case of the octoate. Whereas at the ordinary temperature apparently negative concentrations are deduced for colloid owing to the influence of hydration, even up to 0·6*N*-solution, at 90° the negative value at 0·2*N* is almost within the experimental error, and the formation of colloid shown already at 0·5*N*-solution to the extent of 14 per cent.

The Formulation and Concentration of the Ionic Micelle.

As was shown in the previous communication, the conception of the ionic micelle that appears most probable pending the results of further experiments is that it consists essentially of an aggregation of ordinary ions retaining their original charges. Around this nucleus would be condensed a large number of molecules of water, and probably also most of the neutral colloidal soap available. This is represented in the formula

$$(\mathrm{NaP})_x(\mathrm{P})_n^{n(\prime)} \,.\, (\mathrm{H_2O})_m.$$

With increasing concentration, or when the dissociation is diminished, this must tend to alter towards neutral colloid

$$(\mathrm{NaP})_x \,.\, (\mathrm{H_2O})_m.$$

There was evidence for the conclusion that hydration diminishes and mobility increases with increasing concentration.

We have shown how the approximate values of the concentra-

tions of the total crystalloid and total colloid can be obtained. We have now to allocate the total crystalloid between undissociated soap, sodion or potassion, and simple fatty ion, and the total colloid between neutral colloid, $(NaP)_x$, and aggregated ions in the micelle, $(P)_n^{n(')}$.

This is at present possible only between certain limits set out in table XII below. The first figure in each pair allocates the total colloid so far as possible to micelle; this cannot, of course, exceed the concentration of potassion or sodion, and any excess must necessarily be ascribed to neutral colloid. The second figure in each case makes the opposite assumption, allotting the total colloid to neutral colloid as far as possible. The maximum here is the total amount of undissociated soap obtained by subtracting the concentration of potassion or sodion from the total concentration of the solutions; any excess of colloid must then be recognised as ionic micelle. Table XII includes previous data for the case of potassium laurate at 90° for comparison. Results are expressed in mols. per 1000 grams of water.

TABLE XII.

Measured Limits of Concentration of Constituents of Soap Solutions.

N_w.	Neutral colloid, $(KP)_x$	Micelle, $P_n^{n(')}$	Simple ion, P'.	Simple undissociated KP.	Cation. K.
		Potassium Octoate at 0—18°.			
1·0	0·00—0·14	0·14—0·00	0·35—0·50	0·50—0·35	0·50
2·0	0·31—1·13	0·82—0·00	0·04—0·82	0·82—0·04	0·82
		Potassium Laurate at 0—18°.			
0·1	0·01—0·04	0·03—0·00	0·00—0·03	0·06—0·03	0·03
0·2	0·06—0·13	0·07—0·00	0·00—0·07	0·07—0·01	0·07
0·4	0·24—0·26	0·14—0·11	0·00—0·03	0·03—0·00	0·14
0·5	0·30—0·32	0·18—0·16	0·00—0·02	0·02—0·00	0·18
0·6	0·36—0·39	0·21—0·18	0·00—0·03	0·03—0·00	0·21
1·0	0·60—0·64	0·36—0·32	0·00—0·04	0·04—0·00	0·36
2·0	1·21—1·34	0·66—0·53	0·00—0·06	0·13—0·07	0·66
		Potassium Laurate at 90°.			
0·2	0·00	0·00	0·10	0·10	0·10
0·5	0·00—0·22	0·22—0·00	0·04—0·26	0·24—0·02	0·26
1·0	0·33—0·48	0·52—0·37	0·00—0·15	0·15—0·00	0·52
2·0	1·00—1·11	0·89—0·78	0·00—0·11	0·11—0·00	0·89

TABLE XII. (*continued*).

Measured Limits of Concentration of Constituents of Soap Solutions.

N_w.	Neutral colloid, $(KP)_x$.	Micelle, $P_n^{n(')}$.	Simple ion, P'.	Simple undissociated KP.	Cation. K.
		Potassium Oleate at 0—18°.			
0·1	0·05—0·08	0·02—0·00	0·00—0·02	0·02—0·00	0·02
0·2	0·14—0·15	0·05—0·04	0·00—0·01	0·01—0·00	0·05
0·4	0·28—0·29	0·11	0·00	0·00	0·11
0·5	0·35—0·36	0·14	0·00	0·00	0·14
0·6	0·41—0·43	0·17—0·16	0·00—0·01	0·01—0·00	0·17
		Sodium Oleate at 0—18°.			
0·2	0·15—0·16	0·04—0·02	0·00—0·01	0·01—0·00	0·04
0·4	0·32	0·08	0·00	0·00	0·08

An inspection of the data in table XII reveals that in the cases of the oleates and the more concentrated solutions of the laurates, the limits of concentration of each constituent are narrowly defined. These solutions consist almost entirely of colloid, together with potassion or sodion. There is more than twice as much neutral colloid, $(KP)_x$, as of agglomerated ions, $P_n^{n(')}$; in these potassium soaps and in sodium oleate there is four times as much $(NaP)_x$ as of $P_n^{n(')}$, whereas at 90° the proportion varied between 3/2 and nearly equal amounts.

Once more the difference between potassium and sodium soaps asserts itself, a difference that is evidence for the inclusion of the neutral colloid in the micelle, since otherwise the micelle must be of identical composition in the two cases. Although there is the same total amount of colloid in both cases, the sodium soap contains only about half as much micelle.

Comparison with solutions at higher temperatures shows that there is more neutral colloid present at low temperatures, presumably in the micelle, and possibly in the same way that there is also greater hydration at the lower temperature. This accords also with the abnormally high temperature-coefficient of conductivity.

Comparison with Results of Dew-point Measurements at 20°.

We have carried out a few dew-point measurements at 20° for comparison, employing the method previously described. The data

are given in table XIII. It will be noticed that the data agree exactly with the most accurate of the freezing-point data; the method is applicable at all temperatures, and therefore to all soap solutions.

TABLE XIII.

*Measurements of Lowering of Dew Point of Soap Solution.**

Soap.	N_w.	Temperature.	Lowering.	Crystalloid.	"i."
Potassium chloride	1·0N	20°	0·58°	1·99	1·99
„ laurate.....	0·2	20	0·04	0·14	0·70
„ octoate	3·0	20	0·70	2·41	0·99
„ oleate	0·6	20	0·07	0·24	0·40
0·2 Potassium laurate + 0·6 „ oleate	—	20	0·12	0·41	0·51
Ammonium laurate	1·0N	20°	0·17°	0·583	0·583
„ „ ...	0·5	20	0·08	0·275	0·55
„ palmitate ...	1·0	20	0·06	0·206	0·21
„ „	1·0	90	0·13	0·277	0·28

The complicated effect possible when soaps are mixed in solution has been discussed elsewhere. In the case of the mixture in table XIII, 0·6N in respect of oleate and 0·2N in respect of laurate, the total concentration of crystalloid is 0·41N, as compared with 0·38N, the sum of that of the constituents separately. The conductivity of the mixture is also 5 per cent. above that of the constituents, so that most of this increase may be attributed to formation of mixed ionic micelle.

Ammonium Soaps.

The study of ammonium soap prepared from palm-kernel oil (which is largely laurate with some higher constituents) by Goldsmidt and Weismann (*Kolloid Zeitsch.*, 1913, **12**, 18) has given very interesting results. Like the potassium soaps, they exhibit fairly high conductivity, which in this case cannot possibly be due to products of hydrolysis. The conductivity curve differs greatly from those of sodium and potassium soaps in that it rises steadily with concentration from 0·2N- up to 1·0N-solution by about 38 per cent. The rise is rapid at first, then more gradual. Dilute solutions were not measured. The rise is accompanied by an increase in viscosity of several hundred-fold. All these solutions are appreciably hydrolysed, as is shown by the increase in conductivity effected by addition of excess of ammonia, which in itself is a poor conductor.

These results can be interpreted as showing that the simple fatty

* Measurements by M. E. L.

ion existing in more dilute solutions is being replaced in more concentrated solutions by the ionic micelle, which is a better conductor. This is quite in accord with our conclusions, but the micelle in concentrated solutions must conduct as well as a good conducting ion, such as potassion.

Some dew-point measurements of ammonium soaps are given in the lower half of table XIII. The solutions were prepared from pure fatty acids. It was not considered necessary to correct them for the effect of the partial pressure of the ammonia, as it was evidently too small.

In warm weather, the *N*- and *N*/2-laurates were quite clear solutions showing none of the usual appearances of soap solutions except that they gave a very good lather. On cooling, the *N*/2-laurate solution deposited feathery, crystal-like flakes; the *N*-solutions did not do this, but in very cold weather they set to a semi-transparent jelly similar to a potassium soap. The *N*/2-palmitate was somewhat similar, but the *N*-solution was practically solid at all temperatures, and resembled solid white foam.

A glance at the results shows that, independent of the temperature, there is a very large difference between ammonium laurate and palmitate—very much greater than that observed in potassium soap solutions. The total crystalloid in ammonium laurate is nearly 50 per cent. greater than in potassium laurate, whereas in ammonium laurate it is much less than in ammonium palmitate. An appreciable fraction of the total crystalloid will be undissociated ammonia.

Further investigation would evidently be well repaid, particularly if pure fatty acids were used for making the solutions and hydrolysis were avoided, as suggested above. Enough has been presented to show that the relationships agree with our general conception of colloidal electrolytes.

General Conclusions and Summary.

The theory of colloidal electrolytes defined by one of us receives further confirmation from the measurements of conductivity, freezing point, and vapour pressure of soap solutions at the ordinary temperatures here communicated.

The general theory is based on the conception, justified on mechanical grounds, that ions may be aggregated to form the nucleus of a colloidal particle, termed the ionic micelle, whilst retaining their equivalent electrical charges. Thus the ionic micelle exhibits conductivity as well as mobility even greater than the ions contained in it.

In the case of soap solutions, such as those of potassium oleate, the ionic micelle in concentrated solutions exhibits an equivalent conductivity three times greater than the oleate ion and equal to that of the potassion. Its general formula may be taken as $(KOl)_x . (Ol)_n^{n(-)} . (H_2O)_m$, the amount of water of hydration involved being least in concentrated solutions and at higher temperatures. The change in hydration explains the abnormal temperature-coefficient of conductivity.

The formation of colloid, in the case of higher soaps, is so complete at the ordinary temperature that in all ordinary solutions the only other constituent is the potassion, sodion, or ammonion, as the case may be. In dilute solutions, the soaps become simple crystalloidal salts, and hydrolysis becomes appreciable.

No other representative of this very numerous and important group of substances has yet been completely investigated, but the data available for such instances as the silicates, tellurates, dyes, proteins, salts of alkaloids, gelatin, or casein, etc., agree with the requirements of the theory, which affords a fresh interpretation and reconciliation of the results.

In conclusion, we desire to express our thanks to the Colston Society of the University of Bristol for substantial grants towards the purchase of materials and apparatus.

CHEMICAL DEPARTMENT,
THE UNIVERSITY, BRISTOL. [*Received, September 17th*, 1919.]

CXX.—*The Degree of Hydration of the Particles which Form the Structural Basis of Soap Curd, Determined in Experiments on Sorption and Salting Out.*

By JAMES WILLIAM McBAIN and MILLICENT TAYLOR.

IN 1911 we published experiments on the salting out of sodium palmitate by sodium hydroxide, the results of which appeared to us highly remarkable (*Zeitsch. physikal. Chem.*, 1911, **76**, 199, table IX). When the sodium palmitate was salted out, the clear solution that remained as mother liquor, or lye, contained a higher concentration of sodium hydroxide than before.

The explanations advanced were either that the curd which was salted out contained some acid sodium palmitate, or that very

pronounced negative sorption had occurred; and further experiments to decide this were outlined.

It is the object of this communication to present the results of the first of a series of investigations which show that salted out sodium palmitate is hydrated, and that the curd as a whole consists of this hydrated solid together with entangled or enmeshed mother liquor.

It is impossible to elucidate this problem merely by the direct analysis of the curd, since the curd contains a quantity of concentrated lye mechanically entangled, and yet cannot be washed.

If acid soap were present, it would nevertheless be entirely masked by the large amount of free alkali in the solution clinging to it. Methods had to be devised for distinguishing the water chemically or physically combined (sorbed) from that of the enmeshed solution, thus affording a knowledge of the composition of the curd itself.

In carrying out the present experiments the concentration of the lye before and after salting out was determined, and this was supplemented by a complete analysis of the wet curds. The calculation is based upon the assumption that the sodium hydroxide is not appreciably sorbed by the hydrated curd. As will be shown, this leads to values which are only slightly less than the true degree of hydration. Methods of preparation employed and precautions observed were those previously described.

The Method of Calculation of Hydration from Analysis of Lyes.

If a system is made up by taking 1 mol. of sodium palmitate (NaP) and 1000 grams of water and 2 mols. of sodium hydroxide (thus 2·000 weight-normal, N_w) and the curd separates out quantitatively with, say, a composition corresponding with $NaP,5H_2O$, 5 mols. of water will have been abstracted from the lye. The removal of $5 \times 18{\cdot}02 = 90{\cdot}1$ grams of water from the 1000 grams originally present will have resulted in an increase of the weight-normality of the solution of sodium hydroxide from the value $N = 2{\cdot}000$ to a normality N', where

$$N' = \frac{1000}{1000 - 90{\cdot}1} N.$$

Hence, in general, if W is the weight of water abstracted,

$$W = 1000\left(1 - \frac{N}{N'}\right) \text{ grams.}$$

If the weight-normality of the original sodium palmitate had been

N_s, the hydrate or sorbed water abstracted by N_s mols. of sodium palmitate would have been

$$\frac{W}{18{\cdot}02 \times N_s} \text{ mols. of water,}$$

or

$$\frac{1000}{18{\cdot}02 \times N_s}\left(1 - \frac{N}{N'}\right) \text{ mols. of water to one of NaP.}$$

The residual sodium palmitate in solution in the lye amounted to only a few ten-thousandths normal, which does not affect the results.

Actually in most of the experiments, pure palmitic acid was weighed into a large silver tube and a measured volume of a concentrated solution of sodium hydroxide was added. After sealing with pure silver the tube was placed in a thermostat at about 90° and shaken during periods ranging from ten days to three months. The contents were then filtered through perforated silver foil at 90°. In carrying out the calculation outlined above, the water formed by the chemical reaction between the palmitic acid and the sodium hydroxide was taken into account, and volume was converted into weight-normality.

Hydration Results from Analysis of Lyes.

Table I presents the data of ten experiments in which sodium palmitate was salted out by sodium hydroxide. The first column contains the number of the experiment for further reference; the second, the total amount, in mols., of palmitate in 1000 grams of water, calculated as sodium palmitate; the third, the amount of sodium hydroxide in excess; the fourth, the time allowed for interaction; the fifth, the weight-normality of the sodium hydroxide in the lye after the experiment; the sixth, the amount of sorbed water to 1 mol. of sodium palmitate. In experiment 3 (*a*) previously prepared pure sodium palmitate was added to the hydroxide; in all other cases palmitic acid was added direct.

TABLE I.

Hydration of Sodium Palmitate Curds at 90°.

	Original charge.				
No. of expt.	NaP. N_s.	NaOH. N.	Time shaken.	Lye, NaOH N'.	Hydration: mols. H_2O to 1 NaP.
1*a*	0·9823	2·9470	10 days	3·119	3·1
10	0·9939	2·9816	4 weeks	3·2189	3·7

Mean hydration = 3·4 H_2O.

TABLE I. (*continued*).

Hydration of Sodium Palmitate Curds at 90°.

No. of expt.	Original charge. NaP. N_s.	Original charge. NaOH. N.	Time shaken.	Lye, NaOH N'.	Hydration: mols. H_2O to 1 NaP.
1	0·9608	1·9215	4 months	2·084	4·5
3	0·9608	1·9216	3 ,,	2·1004	4·9
6	0·9337	1·8675	10 weeks	2·042	5·0
7	0·4949	1·7919	10 ,,	1·898	6·3
				Mean hydration = 5·2 H_2O.	
3*a*	0·5021	1·5065	14 days	1·611	7·2
2*a*	0·495	1·485	10 ,,	1·596	8·0
11	0·5002	1·5006	4 weeks	1·566	4·7
12	0·5145	1·589	4 ,,	1·686	6·2
				Mean hydration = 6·5 H_2O.	

The results recorded in table I show clearly that there is a definite amount of combined water in each case, and that this depends on the concentration of sodium hydroxide present in equilibrium with the curd. Thus for 3·0, 1·9, and 1·5*N*-sodium hydroxide solutions the hydration is 3·4, 5·2, and 6·5 mols. of water to 1 mol. of sodium palmitate. In other words, halving the concentration of the lye has doubled the degree of hydration.

Of course, if some sodium hydroxide also is combined in the curd, the above numbers have to be slightly increased to give the true hydration values.

The result found for curd in the presence of 1·9*N*-sodium hydroxide is confirmed by an analysis of the curd itself. One hundred grams of curd contained 57·66 grams of sodium palmitate, 1·681 grams of sodium hydroxide, and 40·66 grams of water; or, to 1 mol. of sodium palmitate, 0·2027 mol. of sodium hydroxide and 10·89 mols. of water. Since the lye was shown to be 1·898*N*-sodium hydroxide, 5·93 mols. of water are to be regarded as solvent (enmeshed lye). This leaves 5·0 mols. of water of hydration to 1 mol. of sodium palmitate, as compared with the mean result, 5·2 mols., given in table I. Again, it is of interest to note that this curd contained about equal amounts of enmeshed lye and combined water.

Two further results are given in table II. Here the solution employed for salting out contained 2*N*-sodium chloride together with *N*/2-sodium hydroxide and previously prepared sodium palmitate.

The headings of the columns are as in table I, except that a

column giving the original normality of sodium chloride has been inserted after the third.

TABLE II.

Hydration of Sodium Palmitate at 90°.

No. of expt.	Original NaP.	Charge NaOH	NaCl.	Time shaken.	Lye NaOH.	Hydration mols H_2O.
15	1·100	0·5069	2·000	2 weeks	0·5508	4·4
16	1·000	0·5069	2·000	14 days	0·5508	4·4

Mean hydration = 4·4 H_2O.

This result, $4{\cdot}4H_2O$ to 1NaP, where the lye is $2{\cdot}5N$ altogether, agrees excellently with the values in table I, and would make it appear that the hydration of the curd may be governed more by the concentration of the lye than by the nature of the salt employed in salting out. If this proves to be the case it will only be necessary to ascertain the molar concentration of soap lye in order to measure the hydration of commercial soap curds, once a standard value for each type has been obtained.

Results with sodium stearate are given in table III, showing that with $1{\cdot}4N$-sodium hydroxide the mean hydration is about $4{\cdot}3H_2O$, as compared with $6{\cdot}5H_2O$ for the palmitate.

TABLE III.

Hydration of Sodium Stearate Curd at 90°.

No. of expt.	Original Na stearate.	Charge NaOH.	Time shaken.	Lye NaOH.	Hydration mols. H_2O.
13	0·4679	1·404	46 days	1·444	3·3
14	0·4679	1·404	48 „	1·469	5·3

Mean hydration = 4·3 H_2O.

The Effect of great Pressure on the Hydration of Soap.

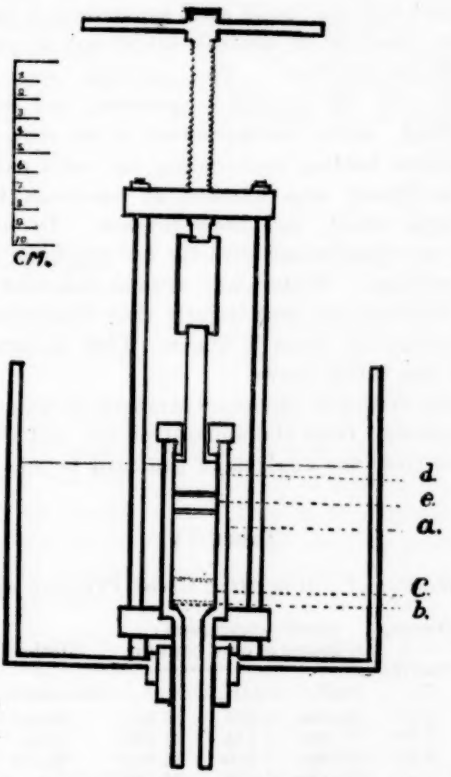
In order to leave no loophole for the alternative explanation of the phenomena here considered, experiments were carried out in which the curd was subjected to a pressure of hundreds or thousands of atmospheres during filtration. The lye filtering through was, of course, concentrated sodium hydroxide, and if the solid part of the curd really contained acid sodium palmitate, and if the separation from the curd was carried far enough, analysis of the residual curd must show a direct deficiency of alkali. However, we found that the curd was always alkaline, no matter how extreme the pressure or how much lye had been forced out. The only observed effect of applying pressure to the curd, whilst allowing the lye to escape, was to diminish the amount of hydration.

The press employed, together with the thermostat in which it was

fixed, is sketched in cross-section in the figure. The filter bed consisted essentially of sugar-carbon previously treated with lye, but arranged so as to avoid contact with the soap curd as far as possible.

The filtration was carried out in the steel tube *a*, fitted with a perforated steel filter disk, *b*.

On the top of this disk was a sheet of nickel gauze, and above



Press employed for diminishing the hydration and imbibition of soap curd.

that again a layer of perforated silver foil. The carbon bed, *c*, some 1—1·5 cm. in depth, rested on the foil and was covered with two more layers of the perforated silver foil. Before use the whole bed was moistened with lye and made thoroughly compact by pressure from the piston *d*.

The soap curd from which the lye had been rapidly filtered, through a silver cone, at 90°, was transferred to the filter and covered with two layers of perforated silver foil. Between this and

the steel piston was inserted a hollowed out, thick-walled rubber washer of the form used in a Bramah press. Pressure was applied through the screw by means of a double set of levers, about 80 cm. in length.

The sample of curd for analysis was taken from the centre of the block of hard curd left in the press. In satisfactory experiments it contained no carbon. Various methods were employed in the analysis, but only the one found most convenient is here described.

The curd was dissolved in neutral, boiled-out 80 per cent. alcohol containing phenolphthalein. The solution was titrated with $N/10$-sulphuric acid, the alcohol evaporated, and excess of N-sulphuric acid added. After decomposition of the soap had been completed by alternate heating and cooling, the solid palmitic acid was collected. The filtrate was titrated to ascertain the amount of sodium palmitate which had been present. In many cases the palmitic acid was determined directly by weighing or by titration in alcoholic solution. Water was always obtained by difference. The method of calculation was usually that illustrated by the curd analysis accompanying table I above. This is termed "mixed" calculation in the table above.

In a few cases, however, the concentration of lye after salting out was not determined. Here the amount of lye and its concentration were calculated from the analysis of the curd by successive approxi-

TABLE IV.

Hydration of Curds after Great Pressure at 90°.

No. of expt.	Original charge. NaP. N_p.	Original charge. NaOH. N.	Curd composition: 100 grams of curd contain NaP.	NaOH.	H_2O.	Method of calculation.	Hydration: mols. H_2O: to 1NaP.
10	0·994	2·98	83·644	0·899	15·457	"Mixed"	1·547
4	0·997	1·99	77·580	1·154	21·266	"Curd"	1·42
1	0·961	1·92	(73·850	1·286	24·864)	"Mixed"	2·0
			(74·424	1·383	24·193)		1·6
2	0·961	1·92	(69·99	1·021	28·994)	"Curd"	3·6
			(67·23	1·306	31·479)		3·5
			(77·51	1·153	21·342)		(1·3 pressed on tile)
3	0·961	1·92	66·146	1·235	32·619	"Mixed"	4·3
6	0·934	1·87	(68·404	1·329	30·267)	"Mixed"	3·3
			(67·616	1·314	31·070)		3·4
			(81·913	2·084	16·003)		—1·8 (pressed on tile)
7	0·495 Sodium stearate	1·79	73·804	0·785	25·411	"Mixed"	3·2
13	0·468	1·404	70·682	1·227	28·091	"Mixed"	1·6
14	0·468	1·404	72·916	0·905	26·179	"Mixed"	2·5

mations based on the hypothesis that all excess of hydroxide was contained in the lye and not in the curd proper. As may be shown theoretically, this leads to a perfectly defined result for the value of the hydration. This we term the pure "curd" calculation.

The results for sodium palmitate salted out by sodium hydroxide are given in table IV. The pressure was different in each case, since it depended on the condition of the filter bed, pressure being applied until the curd began to be forced through. (In one or two cases some carbon was mixed with the curd.) Several samples at different levels were taken for analysis in some of the experiments. Table V gives similar data for the pressed curds of Experiments 15 and 16 of table II.

TABLE V.

No. of expt.	Curd composition: 100 grams contain NaP.	NaOH.	NaCl.	Method of calculation.	Hydration: mols. H_2O to 1 NaP.
15	80·01	0·144	0·761	"Mixed"	2·2
16	80·43	0·160	0·922	"Mixed"	2·2

On examining the results of tables IV and V it appears that the very great pressure to which the curds were subjected while in contact with residual lye lowers the degree of hydration to about half of that of the unpressed curd. This is in accordance with the recognised property of colloids that the swelling pressure increases enormously as the solvent is removed, although the pressures here employed far transcend those hitherto investigated.

The most effective way of dehydrating soap curd is to press it on a porous tile, thus making use of the swelling pressure of kaolin to abstract the water. Curds from Experiments 2 and 6 so treated and the composition calculated as before, gave values for apparent hydration of 1·3 and −1·8 mols. of water respectively; this appears to show that the residual lye had also been greatly concentrated in the process owing to hydroxide being left when the water was absorbed.

Summary.

Marked negative sorption of sodium hydroxide occurs when soap is salted out by sodium hydroxide in concentrated solution.

From the extent of this effect the amount of water contained in the solid part of the curd, as distinguished from the entangled lye clinging to it, may be deduced. Soap curd is thus shown to be a mechanical mixture of hydrate (or sorption compound) and enmeshed lye.

The degree of hydration varies with the concentration of lye as follows:

Lye.	Sorption compound.	Percentage of fatty acid.
3·0*N*	$NaP,3{\cdot}2H_2O$	76·28
2·5	$NaP,4{\cdot}4H_2O$	71·67
1·9	$NaP,5{\cdot}2H_2O$	68·89
1·5	$NaP,6{\cdot}5H_2O$	64·81

Extreme pressure lowers the degree of hydration considerably.

In conclusion, we have pleasure in thanking the Colston Society of the University of Bristol for a generous grant towards the purchase of materials and apparatus.

THE CHEMICAL DEPARTMENT,
BRISTOL UNIVERSITY. [*Received, September 17th*, 1919.]

CXXI.—*Reaction of the Potassium Salts of 2-Thiol 5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole and 2 : 5-Dithiol-1 : 3 : 4-thiodiazole with Halogenated Organic Compounds.*

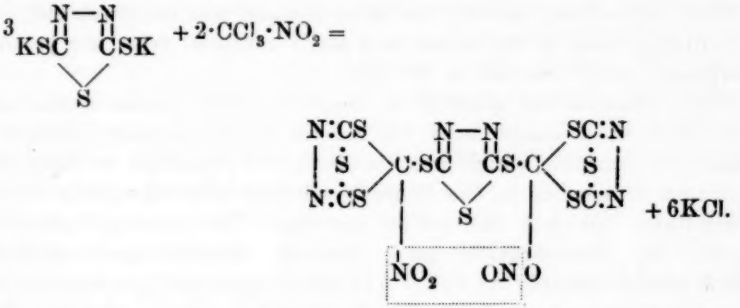
By PRAFULLA CHANDRA RÂY, PRAFULLA CHANDRA GUHA, and RADHA KISHEN DAS.

GABRIEL (*Ber.*, 1877, **10**, 185) and Holmberg (*Ber.*, 1907, **40**, 1740) treated sodium ethylmercaptide with chloroform and obtained ethyl orthotrithioformate, $CH(SEt)_3$. In the present investigation, it will be shown that the potassium atom of the complex cyclic mercaptides named in the title is singularly reactive towards the halogen atoms of organic compounds of divers types. Thus, chloroform, bromoform, and iodoform yield compounds with the potassium monomercaptide, which may be represented by the general equation $3RK + CHX_3 = 3KX + CHR_3$, where X represents a halogen atom and R the radicle of the complex mercaptide. Chloropicrin acts exactly like chloroform, but is far more reactive than the latter, and the reaction may be expressed by the equation $3RK + NO_2{\cdot}CCl_3 = NO_2{\cdot}CR_3 + 3KCl$.

The behaviour of tribromoresorcinol, benzylidene chloride, monochloroacetic acid, and ethylene bromide has also been found to be of an identical nature. The potassium salt of 2 : 5-dithiol-1 : 3 : 4-

thiodiazole, on the other hand, acts almost as an inert substance towards chloro-, bromo-, and iodo-form.

It is evident that the presence of the two ·SK groups of the dimercaptide exercises a sort of inhibitory influence on the halogen atoms. The reactivity of these halogenated compounds can, however, be materially enhanced by substituting the remaining hydrogen atom by a nitro-group. For instance, chloropicrin acts very readily on the dimercaptide even in the cold. The introduction of an additional negative group has thus a marked effect. The reaction may be represented as follows:



Nitrous fumes escape during the reaction, and an atom of oxygen, as shown above, forms the connecting link between the two carbon atoms of the residues of two molecules of chloropicrin.

Ethylene bromide acts on the potassium monomercaptide; only one atom of bromide combines with the potassium atom, resulting in the formation of the compound,

Monochloroacetic acid, benzylidene chloride, and ethylene bromide no doubt act on the dimercaptide, but the products of the reaction are insoluble in the ordinary solvents, and thus cannot be purified.

Experimental.

Potassium Salt of 2-Thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole and Iodoform, Bromoform, and Chloroform.

Three molecular proportions of the mercaptide were treated with one molecular proportion of the halogenated compound in alcoholic solution, the mixture being boiled under reflux on the water-bath for several hours. An insoluble mass was obtained consisting of the potassium haloid and the organic derivative. The solution was

allowed to cool and then triturated with water. The aqueous filtrate on evaporation gave crystals of the potassium haloid. The insoluble portion was dried and dissolved in benzene; on evaporation of the solvent, an oily liquid was obtained, which was redissolved in benzene and precipitated by alcohol as an oil. On keeping, the oil solidified to a yellow powder. As it was difficult to get rid of the last trace of iodoform, the powder was repeatedly washed with alcohol and dried in the steam-oven until the odour of iodoform was no longer perceptible. The substance melted at 66—68°.

With bromoform, exactly the same method was followed, but, as it is highly volatile, the excess was easily removed from the yellow compound, which melted at 66—68°.

When the reaction mixture in alcoholic solution was heated at 210—220° in a sealed tube for several hours, a tarry, resinous mass was obtained, which was collected and dissolved in benzene. Addition of alcohol to the benzene solution gave the same tarry precipitate, but not the yellow powder. The alcoholic mother liquor, on concentration, gave shining, needle-shaped crystals which melted sharply at 62°. Analysis proved this product to be the alcoholate of the compound described above, having the formula $CHR_3,2EtOH$. The yield was very poor, most of the product having evidently become resinified owing to the high temperature employed. No reaction took place when chloroform was heated under reflux with the mercaptide in alcoholic solution. The mixture was therefore heated in a sealed tube as in the case of bromoform. The filtrate, separated from the resinified mass, gave, on evaporation, crystals of the alcoholate melting at 62°:

0·1520 gave 0·2532 CO_2. C = 45·23.
0·1101 „ 11·4 c.c. N_2 at 32° and 760 mm. N = 11·26.
0·1260 „ 0·3532 $BaSO_4$. S = 38·48.*

$C_{25}H_{16}N_6S_9,2EtOH$ requires C = 44·6; N = 10·85; S = 37·50 per cent.

It is thus evident that iodoform and bromoform are more reactive towards the mercaptide than is chloroform.

Compound, m. p. 66—68°, from iodoform:

* It may be necessary to point out that in these compounds the sulphur atom is linked both to an aliphatic and to an aromatic and cyclic residue. Carius's method gave an unusually low result, owing to the formation of sulphonic acid. The excess of nitric acid was therefore neutralised with sodium carbonate and evaporated to dryness and fused in a silver dish. The product was evaporated several times with hydrochloric acid before the addition of barium chloride. Owing to the presence of a large amount of sodium chloride and unchanged sodium nitrate, the result is generally a little too high.

0·0953 gave 0·1502 CO_2 and 0·0202 H_2O. C=42·98; H=2·33.
0·0876 ,, 0·2087 $BaSO_4$. S=41·19.
0·075 ,, 8·3 c.c. N_2 at 24° and 760 mm. N=12·50.
$C_{25}H_{16}N_6S_9$ requires C=43·60; H=2·76; S=41·80; N=12·21 per cent.

The compound from bromoform gave C=43·11; H=2·03; N=12·59 per cent.

Potassium Salt of the Mercaptan and Chloropicrin.

The alcoholic solution of the parent substances was heated at 50° under reflux as before. A bulky, yellow precipitate was obtained; after decanting off the mother liquor, it was washed with alcohol and triturated with water to remove potassium chloride. It crystallised from hot benzene in shining, yellow crystals melting at 128—129°. The reaction was almost quantitative, as was proved by weighing the potassium chloride formed:

0·1140 gave 0·1727 CO_2 and 0·0307 H_2O. C=41·31; H=2·99.
0·0948 ,, 11·4 c.c. N_2 at 32° and 760 mm. N=13·18.
$C_{25}H_{15}O_2N_7S_9$ requires C=40·97; H=2·05; N=13·37 per cent.

Potassium Salt of the Mercaptan and Tribromoresorcinol.

The substances were heated in alcoholic solution as before. The amorphous powder obtained was freed from potassium bromide by water, dried, and dissolved in a mixture of alcohol and carbon disulphide; on evaporation, shining crystals melting at 166° were obtained:

0·0881 gave 0·1458 CO_2 and 0·0236 H_2O. C=45·13; H=2·97.
0·0724 ,, 0·1897 $BaSO_4$. S=36·00.
$C_{30}H_{18}O_2N_6S_9$ requires C=46·03; H=2·30; S=36·55 per cent.

Potassium Salt of the Mercaptan and Benzylidene Chloride.

The components in alcoholic solution were heated under reflux for about an hour. The crystalline product melted at 59—62°:

0·0708 gave 0·1321 CO_2 and 0·0193 H_2O. C=50·87; H=3·03.
0·0849 ,, 8·6 c.c. N_2 at 22° and 760 mm. N=11·02.
0·0974 ,, 0·2550 $BaSO_4$. S=35·83.
$C_{23}H_{16}N_4S_6$ requires C=51·11; H=2·96; N=10·40; S=35·55 per cent.

Potassium Salt of the Mercaptan and Ethylene Bromide.

After heating in alcoholic solution as usual, the insoluble product was freed from potassium bromide by means of water, dried, and dissolved in ether. On evaporation, shining crystals melting at 94° were obtained:

0·1644 gave 0·2183 CO_2. C = 36·21.
0·0812 „ 6·6 c.c. N_2 at 30° and 760 mm. N = 8·97.
0·1303 „ 0·0715 AgBr. Br = 23·35.
$C_{10}H_9N_2BrS_3$ requires C = 36·03; N = 8·40; Br = 24·02 per cent.

Potassium Salt of the Mercaptan and Monochloroacetic Acid.

On mixing the components in aqueous solution, the reaction takes place even in the cold, and is completed on heating. The product crystallises from boiling water in silky needles melting at 145°:

0·1279 gave 0·1935 CO_2 and 0·0414 H_2O. C = 41·26; H = 3·60.
0·1697 „ 15·00 c.c. N_2 at 24° and 760 mm. N = 9·99.
0·1580 „ 0·3495 $BaSO_4$. S = 30·38.
$C_{10}H_8O_2N_2S_3$ requires C = 42·06; H = 2·81; N = 9·86; S = 33·81 per cent.

It is of interest to note that whilst monochloroacetic acid behaves in the above manner, dichloro- and trichloro-acetic acids, on the other hand, behave like strong acids, such as hydrochloric acid, that is, they simply regenerate the original mercaptan.

Potassium Salt of 2:5-*Dithiol*-1:3:4-*thiodiazole and Chloropicrin.*

The components were heated under reflux in alcoholic solution for several hours. Nitrous fumes were evolved and a yellow precipitate was obtained. On cooling, this was collected and washed with alcohol to remove adhering chloropicrin, and then triturated with water to move potassium chloride. The yellow powder was insoluble in nearly a dozen ordinary solvents and in mixtures of some of them. Two different preparations had, however, the same melting point (166—168°) and the same percentage composition:

0·1734 gave 0·1274 CO_2. C = 20·04.
0·0853 „ 14·00 c.c. N_2 at 31° and 760 mm. N = 18·03.
0·0899 „ 0·3907 $BaSO_4$. S = 59·68.
$C_8ON_6S_9$ requires C = 19·83; N = 17·40; S = 59·50 per cent.

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CXXII.—*Equilibria Across a Copper Ferrocyanide and an Amyl Alcohol Membrane.*

By Frederick George Donnan and William Edward Garner.

Donnan and Allmand (T., 1914, **105**, 1941) investigated the distribution equilibrium of potassium and chlorine ions across a copper ferrocyanide membrane. In the method adopted, a solution of potassium ferrocyanide was placed on one side of the membrane and a solution of potassium chloride on the other. The results, whilst affording undoubted confirmation of Donnan's theory (*Zeitsch. Elektrochem.*, 1911, **17**, 572), were complicated by the uncertainty as to the manner of ionisation of potassium ferrocyanide. It was considered that this difficulty would be overcome if solutions of two ferrocyanides were employed on the two sides of the membrane, especially if these salts were ionised to the same extent. In the present investigation, the sodium, potassium, and calcium salts were found to be suitable, and mixtures of these were used to test the validity of the theory.

With a mixture of sodium and potassium ferrocyanides, equilibrium will be set up by an interchange of sodium and potassium ions, since the membrane is not permeable to ferrocyanogen ions. Assuming that the ions obey the laws of ideal solutions, the equation for the equilibrium is given by

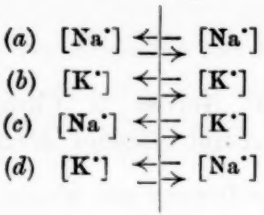
$$[Na_1^{\cdot}][K_2^{\cdot}]=[Na_2^{\cdot}][K_1^{\cdot}],$$

where the symbols indicate molar ionic concentrations.

This equation was derived from thermodynamical considerations by Donnan (*loc. cit.*), and its derivation is also possible from the kinetic theory, as follows: The number of ions of any one kind penetrating the membrane is proportional to its ionic concentration, C_1; the number of ions exchanging across the membrane is proportional, not only to the concentration, C_1, but also to the concentration of the ion, C_2, which interchanges with the first across the membrane, that is,

$$N=K.C_1.C_2.$$

In the case of sodium and potassium ions, at distribution equilibrium four kinds of interchanges across the membrane are possible. Two of these, (*a*) and (*b*) (exchange of like ions), do not affect the final concentrations in any way. The four interchanges are shown below:



At equilibrium, the number of exchanges due to (*c*), that is, $N_c = K[Na_1^{\bullet}][K_2^{\bullet}]$, must equal that due to (*d*), that is, $N_d = K[Na_2^{\bullet}][K_1^{\bullet}]$, therefore $[Na_1^{\bullet}][K_2^{\bullet}] = [Na_2^{\bullet}][K_1^{\bullet}]$.

When the calcium salt is substituted for the potassium salt, the equation of equilibrium becomes:

$$(a)\ [Ca_1^{\bullet\bullet}][Na_2^{\bullet}]^2 = [Ca_2^{\bullet}][Na_1^{\bullet}]^2,$$

and

$$(b)\ [Ca_1][Na_2]^2 = [Ca_2][Na_1]^2,$$

if the degree of ionisation of the two salts is the same.

In the case of the sodium–potassium cells which were investigated, the experimental results showed good agreement with the requirements of the theory.

The degrees of ionisation of the two salts are very similar, so that the ratio of the molar concentrations of the salts is the same as that of the ionic concentrations.

The sodium–calcium cells, however, gave unexpected results. Whereas the equation (*b*), which refers to the concentrations of the two salts, holds within the limit of the experimental error of the analysis, it was found that equation (*a*) above does not accurately represent the relationship between the ionic concentrations of the calcium and sodium salts on the two sides of the membrane. The activities of the ions in this case appear to be more closely related to the molar than to the ionic concentrations. This result also may indicate that adsorption plays an important part in the transference of the ions across the membrane.

Further experiments were carried out in order to find a liquid membrane which would be permeable to one electrolyte and impermeable to a second which contains an ion common to the first. With this purpose in view, the solubilities of several salts in moist, organic solvents were determined. Amyl alcohol was found to be the most satisfactory of these solvents, and potassium and lithium chlorides the most suitable electrolytes. Since lithium chloride is readily soluble in amyl alcohol (a saturated solution is 1·83*N*) and potassium chloride is practically insoluble (a saturated

solution is 0·0048*N*),* it was hoped to set up a cell of the following type:

I. KCl, LiCl in water | Amyl alcohol | LiCl in water II.

which is of the same type as that investigated by Donnan and Allmand with the copper ferrocyanide membrane.

It was not, however, practicable to use an amyl alcohol membrane, owing to the slow rate of diffusion of lithium chloride through the amyl alcohol. The problem was therefore approached in an indirect manner. Determinations were made of the distribution concentrations of lithium chloride between amyl alcohol and water at 25°. Aqueous solutions of lithium chloride and lithium and potassium chlorides were shaken with amyl alcohol, and the two layers separated and analysed. The concentration of the lithium chloride in II, which is in equilibrium with a mixture of the two chlorides in I, was calculated from these results.

The calculation of the ionic concentrations is complicated by the high values of the viscosity of the solutions and by changes in the state of hydration of the lithium ion with concentration. Green (T., 1908, **93**, 2023) has deduced the degree of ionisation of concentrated lithium chloride solutions from measurements of the conductivity of solutions of lithium chloride of which the viscosity has been increased by means of sucrose. The chief objection to the values which are obtained in this way lies in the hydration of the lithium ion, which will be affected by the addition of sucrose to the solutions.

The concentrations of the ions and the undissociated part of the electrolyte have, however, been calculated, using Green's values for the degree of ionisation of lithium chloride, and the results are in fairly satisfactory agreement with theory. The agreement is better in those cases where the total concentration of the electrolytes is below 5*N*. Thus $[LiCl]_1=[LiCl]_2$ and

$$[Li_1^{\cdot}] \cdot [Cl_1'] = [Li_2^{\cdot}] \cdot [Cl_2'].$$

The distribution-coefficient of lithium chloride between amyl alcohol and water has been calculated, and it appears that lithium chloride occurs in amyl alcohol solution as double molecules. The coefficient is, however, only a constant over a small range of concentration, and above 5*N* the coefficient increases. The increase is probably associated with errors in the degree of ionisation due to the dehydration of the lithium ion.

The experimental work in this paper leads to the conclusion that the same equilibrium relationships are established, whether the

* Moist amyl alcohol.

equilibrium is brought about by the transference of ions, as is the case with the copper ferrocyanide membrane, or by the transference of the undissociated part of the electrolyte, as is the case with the amyl alcohol membrane.

Experimental.

The osmometer vessels used in the determination of the ratios of the ions were those described by Donnan and Allmand (T., 1914, **105**, 1944). The copper ferrocyanide membrane in parchment paper was clamped in position between two shallow, cylindrical vessels, and was separated from the supporting rim by rubber bands. The vessels, which were of Jena glass, were fitted with side-tubes to facilitate the introduction of the solutions, and the volume of each vessel was about 100 c.c. The membranes were prepared by the method described by Donnan and Allmand (*loc. cit.*), and the parchment paper was usually left in contact with the solutions for two days. The membranes were tested for leaks by placing a ferrocyanide solution on one side and an isotonic solution of sucrose on the other, and no leakage occurred over a period of six weeks.

The ferrocyanides which were used in the investigation were purified by crystallisation from water. The calcium and ammonia ferrocyanides were prepared from hydroferrocyanic acid (Noyes and Johnston, *J. Amer. Chem. Soc.*, 1909, **31**, 991).

Since potassium ferrocyanide forms insoluble double salts with magnesium and calcium ferrocyanides, of the type

$$R_2K_2FeCy_6,3H_2O,$$

it was not possible to use potassium ferrocyanide against these salts in the cells. The precipitation of the insoluble salts takes place slowly at the ordinary temperature, but quicker on heating, as if a chemical change were taking place. The double salts with sodium ferrocyanide are soluble in water.

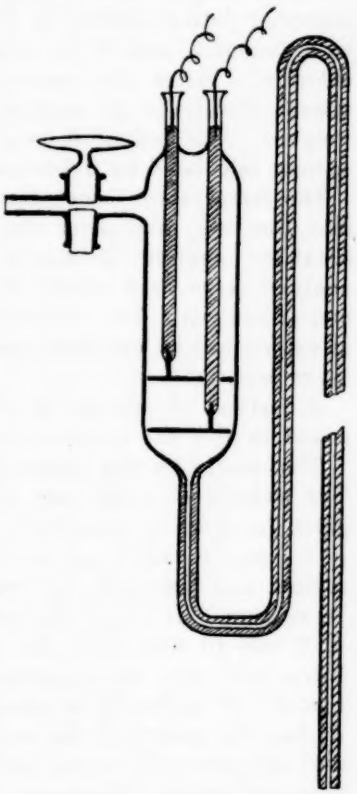
Potassium–Sodium Ferrocyanide Cells.

Solutions were used of a strength 0·025 molar. The usual procedure was to place a solution of potassium ferrocyanide in one side of the cell and a solution of sodium ferrocyanide in the other. The time required for the attainment of equilibrium was determined by conductivity measurements, and no change in the conductivity could be observed after an interval of one week. The cells were, however, allowed to remain, with occasional shaking, over a period of three to five weeks, in which time equilibrium was certain to have been reached.

In order to prevent changes in the ferrocyanide solutions with time, several precautions were necessary.

(1) When pieces of well-washed copper ferrocyanide membrane were placed in solutions of ferrocyanides, it was observed that the strength of the solutions diminished several per cent. in three or four days, and at the same time the presence of sulphates in the solutions was detected. The change was almost entirely due to that side of the membrane which was last exposed to the copper sulphate solution. The adsorbed copper sulphate on this side of the membrane reacted with the ferrocyanide solutions, with the formation of sulphates and a slight increase in the thickness of the membrane. The copper ferrocyanide membrane, after being clamped in position, was on this account washed for three to four days with ferrocyanide solutions of the same concentrations as those to be used in the experiment.

FIG. 1.



(2) Another source of trouble was the oxidation of the ferrocyanides by the small quantity of air enclosed in the osmometer vessels. The oxidation was also considerable if the conductivity of the solutions was measured from time to time in the ordinary conductivity vessels. To make the change due to this cause as small as possible, a special conductivity vessel was constructed (Fig. 1) which could be filled with nitrogen. The amount of air in the osmometer vessel was also reduced to a fraction of a c.c., and in the majority of the experiments, of which the results are given in the tables, the cells were not opened until immediately before analysis.

(3) When solutions of different concentrations were employed on the two sides of the membrane, osmosis of water was prevented by the addition to the solution of the requisite amount of sucrose. The amounts which were added were calculated from conductivity

data. The effect due to this cause is, however, small, as Donnan and Allmand have shown (*loc. cit.*).

The solutions were kept in the dark and the cells shaken every two or three days.

Method of Analysis.

The solutions of the ferrocyanides were decomposed with concentrated sulphuric acid, and the sulphates of the alkali metals converted into chlorides by the precipitation of the iron (twice) with ammonia, and of the sulphate with a slight excess of barium chloride. After the removal of the barium as carbonate, the mixed chlorides in the solution were obtained by evaporisation and weighed. The potassium was determined as perchlorate and the sodium calculated by difference.

The ferrocyanide concentrations were determined before filling into the cells, and after the equilibrium had been reached, by titration against potassium permanganate solution. These analyses serve as a check on the results obtained by the gravimetric analysis. The variation in the ferrocyanide concentrations as determined by the three methods outlined above rarely exceeded 1 per cent.

A method of analysis based on a conductivity method was not found to give the requisite degree of accuracy.

The results for the potassium–sodium cells are given in table I. The weights of potassium chlorate and the mixed chlorides are given (in order to indicate the possible errors of the analyses), and in columns 6 and 7 are included the molar concentrations of the sodium and potassium on both sides of the membrane *A* and *B*. In column 8 is found the total concentration of the metals, and in 9 and 10 four times the total concentration of ferrocyanogen before and after the experiment. The results show that no large amount of oxidation or absorption of the salts has taken place during the period of the experiment. The ratios of the sodium and the potassium in the solutions on the two sides of the cell are compared in the last column, and it will be observed that the ratio is the same for (*a*) and (*b*) within experimental error. The ratio of the ionic concentrations will be but little different from those given in the table, since the degrees of ionisation of the sodium and potassium ferrocyanides are very similar. The conductivity of 0·025 molar solutions of potassium, sodium, and ammonium ferrocyanides was determined at 25°, and the degree of ionisation calculated. The results are given in table II.

TABLE I.

Potassium and Sodium Ferrocyanide Cells.

Cell No.	Weights of				Normality of					
	$KClO_4$.	$\frac{Na}{K}Cl$.	NaCl.	KCl.	Na.	K.	Na + K.	$4Fe(CN)_6$ before.	$4Fe(CN)_6$ after.	$\frac{[Na]}{[K]}$.
1 *a*	0·3123	0·2659	0·0979	0·1680	0·0335	0·0451	0·0786	0·0794	0·0793	0·743
b	0·3145	0·2656	0·0965	0·1691	0·0410	0·0567	0·0977	0·0995	0·0995	0·723
2 *a*	0·2064	0·1992	0·0881	0·1111	0·0503	0·0497	0·1000	0·0990	0·0982	1·012
b	0·2069	0·1982	0·0869	0·1113	0·0496	0·0498	0·0994	0·1000	0·0979	0·996
3 *a*	0·1984	0·1973	0·0905	0·1068	0·0516	0·0477	0·0993	0·1000	0·0998	1·082
b	0·2181	0·2181	0·1007	0·1174	0·0575	0·0524	0·1099	0·1105	0·1095	1·097
4 *a*	0·1839	0·1970	0·0980	0·0990	0·0559	0·0443	0·1002	0·1001	0·1001	1·262
b	0·2163	0·2332	0·1168	0·1164	0·0666	0·05205	0·1187	0·1199	0·1192	1·280
5 *a*	0·1731	0·1935	0·1004	0·0931	0·0573	0·0416	0·0989	0·1005	0·0992	1·377
b	0·1785	0·1993	0·1033	0·0960	0·0884	0·0643	0·1527	0·1506	0·1498	1·375

TABLE II.

Degree of Ionisation of Ferrocyanides.

Salt.	$\Lambda_{\frac{1}{4}=40}$.	Λ_0 Kohlrausch.	100α.
$(NH_4)_4Fe(CN)_6$	383·1	742·0	51·6
$(Na)_4Fe(CN)_6$	337·1	647·6	52·1
$(K)_4Fe(CN)_6$	393·0*	742·0	52·9

* Noyes.

Thus the relationship given below has been proved to be correct, that is,

$$\frac{[Na_1^{\cdot}]}{[Na_2^{\cdot}]} = \frac{[K_1^{\cdot}]}{[K_2^{\cdot}]}.$$

Since the activities of the potassium and sodium ions are probably very similar, the equation deduced by Donnan has been shown to hold.

Sodium–Ammonium Cells.

Ammonium ferrocyanide solutions slowly attack the copper ferrocyanide membrane. The membrane thickens and changes in colour from a dark brown to a reddish-brown. It does not, however, appear to break down, as on one occasion a cell was made up of a solution of ammonium ferrocyanide on the one side and an isotonic sucrose solution on the other. After five weeks, the sucrose solution was tested, and it was found that no ferrocyanide had diffused through the membrane. The concentration of ferrocyanide had, however, diminished, and the colour of the membrane on the one side had changed to a reddish-brown. In consequence of these irregularities, only one sodium–ammonium cell was examined. The ratio $\frac{[Na]}{[NH_4]}$ on the two sides were found to be 0·8480 and 0·8595 respectively.

Sodium–Calcium Cells.

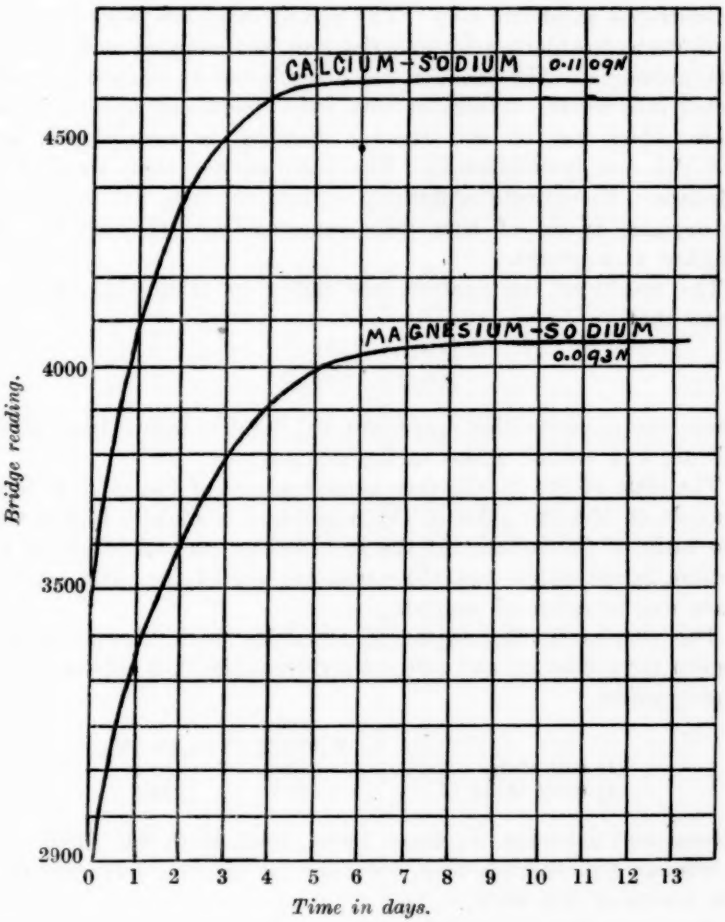
The cells were made up as described previously. The amounts of sucrose used to prevent osmosis were the same as those used with the potassium and sodium solutions of the same concentration. The concentrations of sucrose are probably too great in the case of the calcium solutions, since the calcium salt is less ionised in solution than the potassium salt, but no appreciable osmosis occurred. On the other hand, when the concentrations of sucrose were calculated from Sherrill's equations (*J. Amer. Chem. Soc.*, 1910, **32**, 742), a considerable amount of osmosis occurred.

The rate at which equilibrium is reached is about as rapid as

in the case of the sodium–potassium cells. In some cases, the changes in concentration were followed by conductivity measurements. In Fig. 2 are given the changes of conductivity of a sodium–calcium and a sodium–magnesium cell respectively.

Time in days.	0.	1.	3.	4.	5.	6.	7.	8.	10.	12.
				Bridge-reading.						
Na–Ca	3470	4082	—	4600	—	4635	—	4643	4635	—
Na–Mg	2974	3358	3800	—	3994	—	4040	—	—	4060

FIG. 2.



From the curves and the above table, it will be readily seen that the rate of exchange of sodium and calcium ions is approxim-

ately equal to that of sodium and magnesium ions, and that a constant reading is obtained in about ten days.

The slight fall in the bridge-reading at the end of the experiment (Na–Ca) is probably due to the oxidation of the ferrocyanide.

Method of Analysis.

The analysis of the solutions of calcium and sodium ferrocyanides gave rise to considerable trouble, owing to the small volume (100 c.c.) which was available for analysis. The ferrocyanide solution was evaporated to dryness and decomposed with concentrated sulphuric acid. The mixed sulphates were dissolved in dilute hydrochloric acid, and the iron was removed as hydroxide with ammonia. The calcium was precipitated as oxalate and converted into oxide. Traces of iron were sometimes present in the oxide, which was on this account dissolved in hydrochloric acid and the iron precipitated. The calcium was then weighed as sulphate. The filtrate containing sodium sulphate was evaporated to dryness, traces of iron were removed, and the sodium was weighed as sulphate.

The results of the analyses are shown in table III, and it is found that

$$\frac{[Ca_1]}{[Ca_2]} = \frac{[Na_1]^2}{[Na_2]^2},$$

where the concentrations represent the total concentrations of the calcium and sodium atoms in the solution.

The ratio of the equilibrium concentrations of the calcium ferrocyanide on the two sides of the membrane is slightly higher than the ratio of the squares of the equilibrium concentrations of the sodium ferrocyanide, but the variations are of the same order as those due to errors of analysis.

The change in the degree of ionisation with concentration is known for potassium and calcium ferrocyanides, but not for sodium ferrocyanide.

	100α $K_4Fe(CN)_6$.	$Ca_2Fe(CN)_6$.
(1) 0·05 Molar	48·6	22·1
(2) 0·025 Molar	53·1	23·5

(Noyes and Johnston, *J. Amer. Chem. Soc.*, 1909, **31**, 1010).

Similar figures have been obtained for calcium ferrocyanide in the course of this work.

Assuming that the sodium salt resembles potassium ferrocyanide. and that the ionisation of the mixed sodium and calcium salts is the same as in solutions of the pure salts with concentrations corre-

TABLE III.

Calcium–Sodium Cells.

Cell.	Weight of $CaSO_4$.	Weight of Na_2SO_4.	Normality of 2Ca.	Normality of Na.	Normality of $4Fe(CN)_6$. I.	II.	III.	$\frac{[Ca_1]}{[Ca_2]}$	$\frac{[Na_1]^2}{[Na_2]^2}$	$\frac{[Na_1]}{[Na_2]}$
1 *a*	0·1954	0·2276	0·0573	0·0640	0·1213	0·1196	0·1185	1·265	1·248	1·117
b	0·1541	0·2037	0·0453	0·0573	0·1026	0·1034	0·1029			
2 *a*	0·1673	0·2468	0·0615	0·0867	0·1482	0·1495	0·1473	1·762	1·757	1·326
b	0·1188	0·2324	0·0349	0·0654	0·1003	0·1030	0·1026			
3 *a*	0·1478	0·2064	0·0543	0·0726	0·1269	0·1285	0·1236	1·368	1·332	1·154
b	0·1350	0·2235	0·0397	0·0629	0·1026	0·1049	0·1023			
4 *a*	0·1775	0·2537	0·0652	0·0893	0·1545	0·1534	0·1545	1·802	1·775	1·335
b	0·1231	0·2381	0·0362	0·0670	0·1043	0·1042	0·1032			
5 *a*	0·2189	0·1219	0·1287	0·0686	0·1973	0·2140	0·1995	1·547	1·495	1·223
b	0·2265	0·1595	0·0832	0·0561	0·1393	0·1303	0·1420			

sponding with the ferrocyanogen-ion concentration (Arrhenius), it is possible to calculate the ratios of the calcium-ion concentration and the ratios of the squares of the sodium-ion concentrations on the two sides of the membrane. These are given in the table. The results (table IV) show that the relationship

$$\frac{[Ca_1^{\cdot\cdot}]}{[Ca_2^{\cdot\cdot}]} = \frac{[Na_1^{\cdot}]^2}{[Na_2^{\cdot}]^2}$$

does not hold so strictly as equation (1).

TABLE IV.

Calcium–Sodium Cells.

No.	$\frac{[Ca_1]}{[Ca_2]}$	$\frac{[Na_1]^2}{[Na_2]^2}$	$\frac{[Ca_1^{\cdot\cdot}]}{[Ca_2^{\cdot\cdot}]}$	$\frac{[Na_1^{\cdot}]^2}{[Na_2^{\cdot}]^2}$
1	1·27	1·25	1·25	1·19
2	1·76	1·76	1·68	1·58
3	1·37	1·33	1·33	1·25
4	1·80	1·78	1·73	1·61
5	1·55	1·50	1·49	1·36

The activities of the ions of these two salts thus appear to be more nearly proportional to the molar concentrations than to the ionic concentrations.

Irregularities occurred in two of the cells. Cell 3, which was opened once during the experiment, shows that 2—3 per cent. of oxidation has taken place, and in cell 5 a change, due to osmosis, occurred. Neither of these changes appears to affect the ratio to any great extent.

In cell 5 it should be noted that the concentration of the calcium ferrocyanide is greater than that of the sodium ferrocyanide; in the other cells the reverse is the case.

Amyl Alcohol Membrane.

The results of some preliminary experiments on this membrane are given below.

Materials.—Amyl alcohol (b. p. 131·5°) was obtained by repeated fractionation of fusel oil through a six-bulb fractionating column. One sample of the alcohol was used throughout the work.

The lithium chloride was free from calcium, and was completely soluble in amyl alcohol. Its solution in water was neither acid nor alkaline. It was also analysed by conversion into lithium sulphate, followed by the estimation of the sulphate in this substance, as barium sulphate.

Method.—Aqueous solutions of lithium chloride were shaken with amyl alcohol in stoppered bottles in a thermostat kept at 25°, and when equilibrium had been reached, the two layers were analysed.

Analysis.—The aqueous solutions of lithium chloride were estimated volumetrically with $N/10$-silver nitrate, and the results were checked by analysis of the lithium as sulphate.

A known volume of the amyl alcohol layer was placed in a Jena-glass distilling flask, and the amyl alcohol distilled off. Water was added to the residue, and the solution titrated with silver nitrate.

The solutions containing the potassium and lithium chlorides were analysed according to the method employed by Gooch (*Proc. Amer. Acad.*, 22 N.S. 14, 177). A known volume of the aqueous solution was evaporated in the presence of 10 c.c. of amyl alcohol, and a little hydrochloric acid added to convert any lithium hydroxide into chloride. The lithium chloride dissolves in the amyl alcohol, and potassium chloride is left behind. The residue is collected and washed with hot amyl alcohol. The lithium is then estimated as sulphate, and the potassium chloride dissolved in water and estimated with silver nitrate. To check the results, the solution of the mixed chlorides was titrated directly with silver nitrate.

Results.—The concentrations of lithium chloride in the two layers are given in table V. The concentration of the lithium chloride in amyl alcohol diminishes rapidly with decrease in the concentration in the aqueous solution. The degree of ionisation of lithium chloride solutions cannot be given with any accuracy. The viscosity of the solutions is so great that allowance must be made in the derivation of the degree of ionisation from the conductivity results. Green (*loc. cit.*) has determined the

TABLE V.

*Distribution of Lithium Chloride between Amyl Alcohol and Water.**

$LiCl_{Aq.}$ Total.	$[LiCl]_{Am.}$ Total.	100α.	$[LiCl]_{Aq.}$ undissociated.	$\frac{[LiCl]_{Am.}}{[LiCl]^2_{Aq.}}$
12·54*N*	1·735*N*	36·9	7·91*N*	0·0273
8·49	0·903	47·8	4·43	0·0428
7·77	0·683	50·5	3·85	0·0418
6·68	0·387	54·2	3·06	0·0366
5·00	0·1266	60·1	2·00	0·0277
3·14	0·0342	66·3	1·06	0·0255
3·00	0·0314	66·7	1·00	0·0262
2·71	0·0251	67·7	0·88	0·0268

* In the calculation of the equilibrium constant a correction has been made for the degree of ionisation of the LiCl in the amyl alcohol solution.

viscosity and conductivity of solutions of lithium chloride over a wide range of concentration, and has corrected for the effect of viscosity by the addition of sucrose to the solution. The conductivity at infinite dilution was calculated over a wide range of viscosities; the degree of ionisation is obtained directly from the equation $\alpha=\frac{\Lambda}{\Lambda_f}$, where Λ is the conductivity of a solution of lithium chloride and Λ_f the conductivity at infinite dilution of a solution of lithium chloride containing sucrose, and with the same viscosity as the first solution. Washburn (*J. Amer. Chem. Soc.*, 1911, **33**, 1461) finds that the relation between the degree of ionisation, the conductivity, and the viscosity is given by the relation $\alpha=\frac{\Lambda}{\Lambda_0}\left(\frac{f_0}{f}\right)^m$, where f represents the fluidities and $m=0{\cdot}94$, but this holds only from 0—1·0*N*. For more concentrated solutions, m varies with the concentration. In table VI, m is given for the concentrations

TABLE VI.

Degree of Ionisation of Concentrated Lithium Chloride Solutions.

Normality.	f.	m.	λ.	$100\frac{\lambda}{\lambda_0}\left(\frac{f_0}{f}\right)^m$	100α(Green).
0·0	111·67	—	115·3	—	—
2·0	84·87	0·900	61·63	68·4	69·9
3·0	73·64	0·858	52·58	65·2	66·7
4·0	63·65	0·832	44·76	61·9	63·5
5·0	54·59	0·812	37·85	58·7	60·1
6·0	46·27	0·798	31·70	55·5	56·8
7·0	38·60	0·785	26·04	52·0	53·1
8·0	31·55	0·771	21·05	48·4	49·5
9·0	25·28	0·759	16·725	44·8	46·0
10·0	19·75	0·749	13·225	42·0	43·1
11·0	15·07	0·738	10·395	39·5	40·6
12·0	11·42	0·729	8·149	37·2	38·2

2—12*N*, and the value of m decreases from 0·90 to 0·73. The degree of ionisation calculated from the above equation and the data given by Green will be found in columns 5 and 6. The values are the same as those obtained by Green to within 1—2 per cent. The method of calculation is open to the objection that the lithium ion is probably hydrated in solution, and that the conductivity at infinite dilution, Λ_f, is given by lithium ions, which are probably hydrated to a different extent than is the case in a pure solution of lithium chloride with the same viscosity. The calculated values of the degree of ionisation will therefore be the more accurate for the more dilute solutions.

The values of α in table VI, column 6, are used in tables V and VII. In table V, the amount of undissociated lithium

chloride (column 4) is calculated from these values of α. From the figures in the last column, it will be seen that lithium chloride is associated in amyl alcohol solution to double molecules. A constant for $\frac{[LiCl]_{Am.}}{[LiCl]^2_{Aq.}}$ is only obtained between $2N$ and $5N$. Above this concentration, the coefficient rises from 0·0277 to 0·0428, and then falls. The most probable cause of this deviation is discussed above, and it appears that the calculated concentrations of the undissociated molecules are too low.

The molar concentrations of the solutions of mixed chlorides in I. (p. 1315) and the corresponding equilibrium concentrations of lithium chloride in the amyl alcohol are given in table VII.

TABLE VII.

Results with Amyl Alcohol Membrane.

No.	Total KCl. I.	Total LiCl. I.	LiCl in amyl alcohol.	Total LiCl. II.	Undissociated LiCl I.	Undissociated LiCl II.	[Li·] × [Cl′]. I.	[Li·] × [Cl′]. II.
1	0·944	3·504	0·554	3·78	1·44	1·36	5·94	5·86
2	1·200	2·613	0·303	2·95	0·945	0·976	4·045	3·900
3	0·962	5·45	0·2236	5·80	2·39	2·46	11·02	11·17

From the amount of salt dissolved by the amyl alcohol, and the data in table V, the corresponding values of lithium chloride in II. are calculated and given in column 5. These figures represent the concentrations of lithium chloride in equilibrium with the solution of mixed chlorides in columns 1 and 2 across the amyl alcohol membrane. The ionic concentrations are obtained from Green's values for lithium chloride and from Kohlrausch and Grotrian's values for potassium chloride. The degree of ionisation for the higher concentrations of potassium chloride are obtained by extrapolation from the latter values. The degrees of ionisation of lithium and potassium chlorides are apparently very similar. The ionic concentrations of the solutions of the mixed chlorides are calculated on the assumption made in the case of the calcium–sodium ferrocyanide cells.

Cells 1, 2, and 3 show good agreement with the equations $[LiCl]_1 = [LiCl]_2$ and $[Li_1^{\cdot}][Cl_1'] = [Li_2^{\cdot}][Cl_2']$. The agreement, which is better than would be expected, supports the values for the degree of ionisation of lithium chloride which were obtained by Green.

Summary.

Determinations have been made of the equilibrium concentrations of solutions of sodium and potassium ferrocyanides and

sodium and calcium ferrocyanides across a copper ferrocyanide membrane, and the results are in general agreement with Donnan's theory.

The following cells were investigated:

(*a*) I. Potassium ferrocyanide	Sodium ferrocyanide	II.
(*b*) I. Sodium ferrocyanide	Calcium ferrocyanide	II.
(*c*) I. Sodium ferrocyanide	Ammonium ferrocyanide	II.

The solutions in (*a*), (*b*), and (*c*) were in the neighbourhood of 0·025*N*.

A liquid membrane has been investigated; amyl alcohol was chosen as the most suitable solvent, and the electrolytes employed were potassium and lithium chlorides.

(*d*) I. Lithium chloride Potassium chloride	Amyl alcohol	Lithium chloride	II.

Lithium chloride gives rise to double molecules in amyl alcohol solution, and a constant is obtained for the partition-coefficient up to 5*N*.

So far as the preliminary experiments go, the equilibrium concentrations of the lithium and chlorine ions and the undissociated part of the electrolyte agree with Donnan's theory.

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[*Received, September 22nd*, 1919.]

CXXIII.—*The Colouring Matter of the Red Pea Gall.*

By MAXIMILIAN NIERENSTEIN.

THE colours of oak galls are very varied and rich. They range from white and cream through all tints of yellow to deep orange, from pale green to a rich, dark hue, and through almost every shade of red, some being very beautiful and attractive. These red colours are generally ascribed to the presence of anthocyanins, which are supposed to be derived from the tannins present in galls (compare Gertz, "Studien öfver Anthocyans," 1906; Connold, "British Oak Galls," 1908; Küster, "Die Gallen der Pflanzen," 1911; Magnus, "Die Entstehung der Pflanzengallen," 1914). Our knowledge of the anthocyanins has been fundamentally increased

by the recent investigations of Wheldale, Willstätter, Everest, and others (compare Perkin and Everest, "The Natural Organic Colouring Matters," 1918). Their researches have conclusively proved that the anthocyanins are derived from the different flavones present in plants. This suggested an inquiry into the colouring matter of the so-called anthocyanin of the "red pea gall," frequently found on the leaves of different British oak trees, especially *Quercus pedunculata* when galled by *Dryophanta divisa*, Adler. It seemed reasonable to expect that the anthocyanin of this gall would in all probability be derived from cyanidin, the anthocyanin of quercitin, and, if so, it might furnish some evidence regarding the much discussed question as to the relationship between the pathological products produced by the gall and those normally present in the plant (compare Dekker, "Die Gerbstoffe," 1913). It was, incidentally, also thought possible that an anthocyanin derived from a gall might prove to be closely allied to quercetone or *iso*quercetone, both anthocyanin-like oxidation products of quercetin, described by Nierenstein and Wheldale (*Ber.*, 1911, **44**, 3487) and Nierenstein (T., 1915, **107**, 869; 1917, **111**, 4), as it was probable that the accelerated oxidative processes common to larvæ and imagines (compare Krogh, "The Respiratory Exchanges of Animals and Man," 1916), which, in addition to numerous inquilines, are present in large numbers in galls (compare Connold, *loc. cit.*; Küster, *loc. cit.*), would favour the production of an oxidation product, such as quercetone, and not that of a reduction product, such as cyanidin (compare Everest, *Proc. Roy. Soc.*, 1914, [*B*], **87**, 444).

The investigation of the red colouring matter derived from the "red pea gall" has, however, to some extent proved disappointing. It was found that *dryophantin*, the name suggested for this pigment, was in no way allied either to the flavones or to the anthocyanins, but that it consisted of purpurogallin and two molecules of dextrose. On the other hand, it must be mentioned that purpurogallin has not previously been found in nature. Dryophantin is derived from pyrogallol, like gallotannin, and is therefore of pathological origin, like the latter. Dryophantin, however, cannot be regarded as an anthocyanin, and probably the same can be said of the other so-called anthocyanins derived from plant galls. It is therefore proposed to classify these red pigments in a new group of natural organic colouring matters, to which the name *gallorubrones* is assigned.

Preparation of Dryophantin.

The galls used in this investigation were collected in the vicinity of Bristol and East London during the months of August and September, 1913, 1915, 1917, and 1918, and care was taken to avoid admixtures with the different galls of the *Neuroterus* species frequently met with on the same leaves as the galls of *Dryophanta divisa*. In all, 94 grams of the galls were collected, and the dried material was powdered and extracted in a Soxhlet apparatus, at first with ether and subsequently with chloroform, so as to remove wax, chlorophyll, and the so-called gall-fats. The carefully dried powder was then again extracted in a Soxhlet apparatus with alcohol, which dissolved both the colouring matter and the tannins. The alcohol was distilled off in a vacuum, and the viscid residue redissolved in water. The cold aqueous solution, made up to 150 c.c., was shaken with 5 grams of fat-free caseinogen to remove the tannins (compare Körner and Nierenstein, *Chem. Zeit.*, 1911, **36**, 31), filtered, and extracted with ether. The ether left on evaporation only traces of a tarry substance, apparently a by-product. The aqueous solution was evaporated under diminished pressure at about 55° (water-bath temperature), and the residue dissolved in boiling alcohol and filtered. The red alcoholic extract, after being evaporated to a small bulk, was poured into water, the mixture extracted several times with ether, and the small quantities of alcohol and ether present were removed from the aqueous liquid by prolonged heating on a boiling-water bath. The solution, on cooling, became semi-solid, owing to the separation of crystals; these were collected and washed repeatedly with ether and dilute alcohol. The deep red product obtained in this way was purified by several crystallisations from dilute, and finally absolute, alcohol. The air-dry substance was dried at 130° for analysis, without apparent loss of weight. The total amount of dryophantin thus obtained corresponded with about 4 grams, and there was no apparent difference if fresh or old material (about six months old) was used, which showed that there was apparently no deterioration on keeping.

Found: C = 50·2, 50·4; H = 5·5, 5·4.

$C_{23}H_{28}O_{15}$ requires C = 50·6; H = 5·2 per cent.

Dryophantin was obtained in deep red, glistening needles with a bronzy lustre. It was almost insoluble in cold alcohol, sparingly soluble in hot water, but fairly readily so in boiling methyl and ethyl alcohol, and in larger quantities of boiling acetone. It sintered at 216° and melted at 219—220° to a viscous liquid. The

addition of ferric chloride to its alcoholic solution produced a brick-red precipitate, and a similar precipitate, but slightly darker in colour, was also obtained by the addition of lead acetate. A trace of ammonia turned the alcoholic solution deep blue, which became red on acidification. These colour changes could be produced in an unlimited number of times in the same solution without affecting its sensitiveness to these reagents. Similar blue solutions were also obtained by the addition of sodium, potassium, or barium hydroxides to alcoholic solutions of dryophantin. In this connexion, it must be mentioned that similar colour changes are also given by purpurogallin itself (compare Wichelhaus, *Ber.*, 1872, **5**, 848; Struve, *Annalen*, 1872, **163**, 164; Hooker, *Ber.*, 1887, **20**, 3259). On repeating these observations, it was found, however, that the colour changes are not so permanent in the case of purpurogallin as in the case of dryophantin.

Hydrolysis of Dryophantin.

Experiments having shown that dryophantin was a glucoside, its decomposition with acid was studied in the following manner.

0·5246 Gram, dissolved in 550 c.c. of boiling water, was digested with 5 c.c. of sulphuric acid for two hours. A deep red, crystalline product commenced to separate, and more of it was deposited on cooling. This was collected in a Gooch crucible, washed with cold water so as to remove all traces of sulphuric acid, and dried at 160°. In this way, 0·1928 gram of purpurogallin was obtained.

Found: Purpurogallin = 36·7.

$C_{23}H_{28}O_{15}$ requires purpurogallin = 40·4 per cent.

The low value obtained for purpurogallin is due to its sparing solubility in water, and it was found that the filtrate recovered on hydrolysis of dryophantin to which had been added the washings of purpurogallin contained 2·2 per cent. of purpurogallin, when determined colorimetrically by Willstätter and Stoll's method for the estimation of small amounts of purpurogallin (*Annalen*, 1918, **416**, 46). The total amount of purpurogallin from dryophantin corresponded, therefore, with 38·9 per cent., which is 1·5 per cent. below the theoretical if the hydrolysis of dryophantin is expressed as:

$$C_{23}H_{28}O_{15} + 2H_2O = C_{11}H_8O_5 + 2C_6H_{12}O_6.$$

A second experiment gave 37·1 per cent. of purpurogallin gravimetrically and 1·9 per cent. colorimetrically, corresponding with 39·0 per cent. of purpurogallin, which is 1·4 per cent. below the theoretical.

The purpurogallin recovered from dryophantin was recrystallised from glacial acetic acid, and had the correct melting point of 274—275° generally given for purpurogallin (Found: C=59·8; H=3·7. Calc.: C=60·0; H=3·6 per cent.). The acetyl derivative, which had been prepared by digesting with acetic anhydride, crystallised from alcohol in orange-yellow needles melting at 179—180°, and the melting point was not depressed after mixing with the tetra-acetyl derivative of purpurogallin (Found: C=59·2; H=4·7. Calc.: C=58·7; H=4·1 per cent.).

The filtrate from the first hydrolysis was quantitatively tested for dextrose by Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 915), and the dextrose estimated volumetrically in several portions of the hydrolysate by Bertrand's method (*Bull. Soc. chim.*, 1906, [iii], **35**, 1286), as used by Geake and Nierenstein (*Ber.*, 1914, **47**, 893) for the estimation of dextrose in gallotannin.

Found: Dextrose=62·8, 63·1, 63·0.

$C_{29}H_{28}O_{15}$ requires dextrose=63·3 per cent.

The filtrate of the second hydrolysis was prepared as in the experiment for the quantitative estimation of dextrose, and then concentrated to a small bulk. It was subsequently converted into dextrosazone, which crystallised from dilute alcohol in glistening, yellow needles melting at 203—204° (Found: N=15·8. Calc.: N=15·6 per cent.).

The author begs to acknowledge his indebtedness to the Government Grant Committee of the Royal Society for a grant from which much of the cost of the investigation was defrayed.

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CXXIV.—*The Effect of Salts on the Vapour Pressure and Degree of Dissociation of Acetic Acid in Solution. An Experimental Refutation of the Hypothesis that Neutral Salts Increase the Dissociation Constants of Weak Acids and Bases.*

By JAMES WILLIAM MCBAIN and JAMES KAM.

IN 1899 Arrhenius proposed a modification of his classical dissociation theory to the effect that salts increase the dissociation

constants of weak acids present with them in solution, as if either the water had acquired greater dissociating power or the salt itself was acting as a dissociating medium. The experimental evidence he adduced was the rate of inversion of sucrose by weak acids in the presence of salts.

Arrhenius's idea was very generally accepted and developed, particularly in the field of non-aqueous solutions; but in 1914 it was called in question by McBain and Coleman's re-interpretation of the direct experimental evidence. On recalculation of the data given by Arrhenius, in conformity with present-day conceptions of this reaction, they found that the supposed effect was entirely absent, thus reversing the significance of the experiments. In other words, the dissociation constant of weak acids is not affected by the presence of salts.

They followed this up by a review of all the available experimental evidence bearing on this subject, and they found that it supported only the simple form of the classical dissociation theory.

One isolated group of experiments was left outstanding, inasmuch as in this particular case the measurements were conflicting in their evidence; these were certain determinations of hydrogen ions by the method of electromotive force. The potential of the hydrogen electrode in solutions of acetic acid was greater than that predicted when sodium chloride was present, although this was not the case when sodium acetate was the added salt.

(1) *Object of the Present Investigation.*

The present communication adduces a hitherto unsuspected but general effect of such salts as sodium chloride on undissociated acetic acid, which would account for the apparent results derived from the measurements of hydrogen electrode potential.

The equilibrium under discussion is

$$HAc \rightleftharpoons H^{\cdot} + Ac',$$

where HAc stands for a weak acid such as acetic acid. The potential of the hydrogen electrode in this solution is admittedly too great when sodium chloride is present. This has hitherto been interpreted as a real increase in acidity; in other words, a displacement of the equilibrium to the right—an enhancement of the dissociation constant itself.

The electrical potential of the hydrogen electrode, however, measures the product of the chemical potential and the concentration of the hydrogen ion. Instead of assuming that the increase in this product is due to increase in concentration, we here submit

experimental evidence for the alternative explanation that the other factor, the chemical potential, has been enhanced.

If the concentration of the hydrogen ion has remained unaltered, but its chemical potential or reactivity has been increased, it is necessary for the continuance of equilibrium that the chemical potential or reactivity of the substance on the left-hand side of the chemical equation should likewise have increased. Such increase in reactivity or potential of undissociated acetic acid in the solution must be accompanied by a parallel increase in the partial pressure of acetic acid in the vapour phase.

This is open to direct experimental test, and we find that a remarkable increase is actually exhibited, fully accounting for the electromotive force data observed. This removes the last evidence in favour of Arrhenius's proposed modification of his classical dissociation theory. The effect here discovered has to be taken into account in most determinations of electromotive force.

(2) *The Experimental Method.*

The simple experimental method adopted was the distillation of aqueous solutions of acetic acid with and without addition of various salts.

Pipettes, burettes, and measuring flasks were carefully calibrated. The distillations were carried out in a flask of fused silica of about 1500 c.c. capacity, heated directly by contact with a large Bunsen flame. The neck and upper half of the flask were covered with a lagging of magnesia and asbestos, so as to avoid as much as possible fractional distillation in the flask. The distance between burner and flask was kept constant through all distillations, as was also the flame itself.

The quantity of distilling liquid was each time 1000 c.c., and the distillate was collected in four to five fractions of about 75 c.c. each. After each fraction, the distillation was quickly interrupted for the abstraction of a similar quantity of about 75 c.c. from the residue in the flask; the first residue was abstracted as soon as the liquid began to boil and just previous to the collection of the first fraction of the distillate.

The residues were left to cool in glass-stoppered bottles, vaseline being used on the stoppers to prevent ingress of carbon dioxide from the air.

Samples of 20 c.c. of each of the distillates and residues were titrated against standard solutions of sodium hydroxide of approximately equal strength, with phenolphthalein as indicator; the usual precautions were taken to avoid the vitiating effect of carbonic acid. Thus for each distillate the ratio R_2 could be

determined between the concentrations of acetic acid in that distillate and the mean concentration of acid in the residue in the flask before and after.

Thus the ratio R_2 was determined for solutions of acetic acid of concentrations varying from 0·05 to 0·5N. It appeared that, at least between these limits, R_2 increases only very slightly with the concentration, as is apparent from the curve No. I of Fig. 1, which shows the value of R_2 plotted against the acid concentrations.

The same operations were repeated with solutions of sodium, potassium, and lithium chlorides, potassium thiocyanate, potassium nitrate, sodium sulphate, and sodium acetate in 0·05 to 0·4N-solutions of acetic acid. The concentration of the salts was determined by careful evaporation of 20 c.c. of each residue in a porcelain evaporating dish in a hot-air oven at temperatures depending on the nature of the salt in question. The acetic acid was titrated as before, in distillate and residue, to obtain the ratio R_1 of the concentration.

The values of the ratios R_1 are dependent on the concentration of the salts, but they are independent of the concentration of acetic acid. Sodium acetate differs from the other salts investigated in that it has scarcely any effect on the distillation of acetic acid.

In this manner, values of R_2 derived from a very large number of distillations of solutions of pure acetic acid became the standard of comparison for a number of distillations of acetic acid containing added salts.

The expression $100\ \frac{(R_1 - R_2)}{R_2}$ gives the percentage increase of the ratio R_1 caused by the addition of salt. The experimental data here presented comprise well above one hundred such determinations.

(3) *Method of Calculation of the Distillation Data.*

Distillation was selected for the measurement of the partial vapour pressure of acetic acid merely for the sake of convenience and accuracy. It must be borne in mind that the composition of the distillate shows only the relative proportion of acetic acid and water vapour in the vapour phase above the solution. What is required is the absolute magnitude of the partial vapour pressure of acetic acid at a definite temperature, say 100°. The polymerisation of the acetic acid vapour may be neglected for the present purpose, since it amounts to only a few per cent. at these low

partial pressures. Even this slight effect is largely eliminated in comparing R_1 with R_2.

Ordinary variations in barometric pressure and the concomitant alterations in boiling point have no appreciable influence on the composition of the distillate. Hence, all the distillations may without error be regarded as having been in effect carried out at 100°, even where much salt has been added.

In order to obtain the absolute instead of the relative magnitude of the partial pressure of acetic acid in the vapour distilling over at 100°, the actual partial pressure of the water has to be evaluated. Now, the partial pressure of the water, which in pure water was 760 mm., has been diminished by two effects, for which allowance has to be made.

The first correction may be termed the "osmotic correction." The vapour pressure of the solvent has been reduced in familiar fashion through the osmotic activity of the substance in solution. Hence, in all cases the observed concentration of the acetic acid in the distillate must be diminished accordingly before use. This is readily done with sufficient accuracy for the present purpose by taking the lowering of vapour pressure of the solvent to be 1·80 per cent. per mol. of total solute (ions and undissociated acid and salt).

The second correction is the "volatility correction." It results from the effect of the appreciable partial pressure of the acetic acid in lowering the pressure at which the water actually distils over, instead of this occurring at a partial pressure of water vapour equal to 760 mm. Here again, then, in order to base the relative magnitude of the partial pressure of acetic acid on the constant value of 760 mm. for that of water vapour throughout, the volatility correction has to be applied so as to diminish the observed concentration of the acetic acid in the distillate accordingly. This consists in the reduction of the latter by 0·12 per cent. for a 0·1N-solution of acetic acid, and taking this correction as proportional to the concentration of the acetic acid in the distillate. Since the acetic acid was at most $N/2$, this correction in no case exceeded 0·6 per cent.

A third and final correction had tc be made, this time in the apparent composition of the solution undergoing distillation. This is the "correction for dissociation" of the acetic acid in the solution. The actual ratios measured were those between the concentrations of distillates and the corresponding solutions in the distilling flask (the "residues"). What is required is the ratio based on the actual concentration of undissociated acetic acid in the flask. In the case of solutions containing only acetic acid,

this consisted simply in subtracting the known amount of dissociated acetic acid from the total concentration of acetic acid in the flask. The dissociation constant of acetic acid was taken to be $1{\cdot}11 \times 10^{-5}$ at 100°.

The correction for dissociation involves much calculation where salt is present, since in order to determine the actual concentration of undissociated acetic acid, it is necessary to calculate the amounts of the various ions and undissociated salts present, including those formed by metathesis. For example, with common salt the following molecular species were present: $H^{\cdot}$, Ac', $Na^{\cdot}$, Cl', HAc, HCl, NaCl, and NaAc.

This was done by Arrhenius's method, which is based on the principle of isohydrism (*loc. cit.*), and agrees with the method of Sherrill (*J. Amer. Chem. Soc.*, 1910, **32**, 741). The calculation is laborious and involves successive approximations. Fortunately, the exact degree of dissociation of the various salts has but little influence on the results, since the really important values appear in both numerator and denominator of Arrhenius's equations; conductivity data at the ordinary temperature could therefore be employed failing the existence of such at higher temperatures and concentrations. Indeed, the calculation for solutions of one salt in acetic acid might have been applied to the case of any other salt of the same concentrations, except, of course, in the case of sodium acetate. The effect is chiefly dependent on the relative concentration of acid and added salts.

(4) *The Distillation of Solutions of Pure Acetic Acid.*

Following the method already described, fifteen distillations were carried out with $N/20$- to $N/2$-solutions of acetic acid involving more than seventy determinations. The object in view was to determine the ratio R_2, that is, the ratio, concentration of acid in distillate to concentration of acid in residue.

Thus $$R_2 = \frac{C_d}{C_r},$$

C_d being the concentration of the distillate; C_r being the mean value of the concentrations of the residue before and after the separation of the distillate.

The experimental evidence is summarised in table I. For any one concentration, the results agreed to within 1 per cent. The values of R_2 were corrected as described in Section (3) above, and they increase by only about 1 per cent. over the whole range of concentration. The relative concentration of double molecules, which has not been allowed for, changes from about 5 to 3 per cent. over this same range.

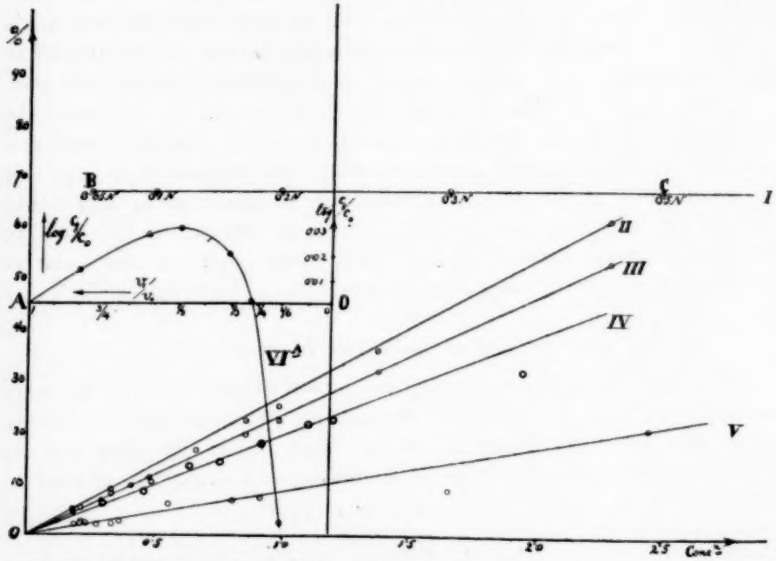
TABLE I. (Curve I.)

Ratio of Concentration in Distillate and Residues in Aqueous Acetic Acid.

Concentration of acid in flask.	R_2 (uncorrected).	R_2 (corrected).
$N/20$	0·662	0·671
$N/10$	0·666	0·671
$N/5$	0·673	0·674
$N/3$	0·680	0·677
$N/2$	0·685	0·678

The corrected values of R_2 increase very slowly indeed. Plotting them against the concentrations, we obtain a straight line (Curve I in Fig. 1).

FIG. 1.



I. $CH_3{\cdot}CO_2H$, *corr.* (B=0·671; C=0·678).
II. NaCl, *uncorr.* *Percentage increase due to salt.*
III. NaCl, *corr.* " " " "
IV. KCl, " " " " "
V. KCNS, " " " " "

VI^A. *Curve*: $\log \frac{C_1}{C_0} = \frac{1}{2{\cdot}3026}\left[\left\{1 - R_2\right\}.\log\frac{v_0}{v_1}.2{\cdot}3026 + R_2.K.\left\{\frac{v_1 - v}{v_1.v_0}\right\}\right]$.
A0 $= v_0 = 1$.

Ratios of acetic acid in distillate and residue with and without added salts.

The corrections for volatility and osmotic effect can be taken from graphs; for example, in the case of $N/20$-acetic acid, they

amount to $-0{\cdot}06$ and $-0{\cdot}09$ per cent. respectively. The third correction for degree of dissociation of the acetic acid is here 1·50 per cent. Thus the total correction in this case is an increase of 1·35 per cent. on the observed ratio $R_2=0{\cdot}662$. Hence we obtain

$$R_2 \text{ (corrected)} = 0{\cdot}662 \times 1{\cdot}0135 = 0{\cdot}671.$$

This value is smaller than the one arrived at by Lord Rayleigh (*Phil. Mag.*, 1902, [vi], **4**, 535), $R_2=0{\cdot}73$. Corrected, it reduces slightly to 0·725, which is still considerably greater (the reduction in this case being caused by the method of calculation of R_2 from the residues). The discrepancy is, however, probably due to the different manner of heating. Lord Rayleigh kept the neck and upper part of the distilling flask hotter than the boiling liquid in order to prevent condensation. We found, however, that this involved the quantitative evaporation of drops splashing up from the boiling liquid, which produces the same error as if they had splashed directly into the distillate. It was for this reason that we relied on good heat insulation and fairly rapid distillation.

Note on the Calculation of the Composition of the Residues at any given Stage of the Distillation of Acetic Acid.

Following Lord Rayleigh (*loc. cit.*), but using concentration of residues expressed in mols. per litre,

$$\frac{C_0}{C_1}=\left(\frac{V_0}{V_1}\right)^{R_2-1},$$

where C_0 and C_1 are the concentrations and V_0 and V_1 the volumes in the distilling flask before and after the distillation.

For example, for $R_2=0{\cdot}671$ and $\frac{C_0}{C_1}=\frac{1}{2}$, $\frac{V_0}{V_1}=8{\cdot}221$. Hence, in order to double the concentration of the residual acid solution in the flask, $\frac{7{\cdot}221}{8{\cdot}221}=0{\cdot}878$, or almost 88 per cent. of the volume of the solution must be distilled over. For $R_2=0{\cdot}73$ (Rayleigh's value in $N/10$-solution), this quantity would amount to 92 per cent.

Again, if 40 per cent. of the original volume of solution is distilled off, that is, if $V_1=0{\cdot}6\,V_0$, $\frac{C_1}{C_0}=1{\cdot}183$, which means that the concentration of the residue will have increased by 18·3 per cent.

(5) *The Experimental Data for Added Salts.*

Having determined the ratios R_2 for solutions of acetic acid, the corresponding ratios, R_1, were obtained in exactly the same manner, but with a salt added to the solution.

The salts used were the purest obtainable in 1913, and are named in Section (2) (above).

The distillates were in each case tested for traces of the stronger acid formed by metathesis, but these were found to be negligible. The corrections were calculated and applied in the same manner as before, except that the acetic acid destroyed by metathesis was calculated according to Arrhenius's principle of isohydrism (*Zeitsch. physikal. Chem.*, 1899, **30**, 208).

The results are summarised in tables II—VIII, which require no further explanation, except to note that in tables II and VII space is saved by averaging the figures for all the values obtained over certain ranges of concentration. The number of experimental values so averaged is given in the last column.

With the exception of sodium acetate, all these salts cause a remarkable increase of the ratio $\frac{C_d}{C_r}$, and sodium chloride shows this increase more than any other of the salts investigated. Sodium acetate, on the other hand, appears to have no appreciable effect even in 1·0*N*-solution.

Tables II.—VIII.

Ratios R_1 *of Concentration of Distillates and Residues of Aqueous Acetic Acid with added Salts, and Increase thereof over* R_2 *of Table I.*

Table II. (Curves II. and III.). *Sodium Chloride.*

HAc.	Salt.	R_1.	R_2.	R_1 (corr.).	R_2 (corr.).	$100\left[\frac{R_1-R_2}{R_2}\right]$	Expts.
0·1—0·2	(0·12)	0·688	0·669	0·690	0·673	2·6	7
0·1—0·3	(0·21)	0·708	0·671	0·710	0·673	5·4	16
0·1—0·3	(0·29)	0·721	0·672	0·716	0·673	6·6	15
0·1—0·3	(0·41)	0·742	0·671	0·721	0·673	9·6	4
0·13	0·661	0·790	0·668	0·715	0·671	16·9	1
0·076	1·04	0·830	0·663	0·820	0·671	22·2	1
0·078	1·38	0·904	0·664	0·885	0·671	32·1	1
0·077	2·30	1·076	0·664	1·033	0·671	53·9	1

Table III. (Curve IV., Fig. 1). *Potassium Chloride.*

0·22	0·2—0·3	0·7146	0·673	0·7111	0·674	5·55	4
0·2540	0·4673	0·7389	0·675	0·7309	0·675	8·20	1
0·2157	(0·70)	0·7741	0·673	0·759	0·674	13·55	2
0·2053	0·9228	0·8121	0·673	0·7930	0·674	17·70	1
0·22	1·17	0·8383	0·673	0·8133	0·674	21·55	2
0·2194	1·953	0·9363	0·673	0·8872	0·674	31·60	1

Table IV. (Curve V., Fig. 1). *Potassium Thiocyanate.*

0·2—0·23	0·2—0·34	0·6900	0·673	0·6868	0·674	1·90	6
0·2673	0·5590	0·7297	0·675	0·7181	0·675	6·40	1
0·2366	1·663	0·7693	0·674	0·7343	0·674	8·90	1
0·2595	2·451	0·8710	0·675	0·8112	0·675	20·10	1

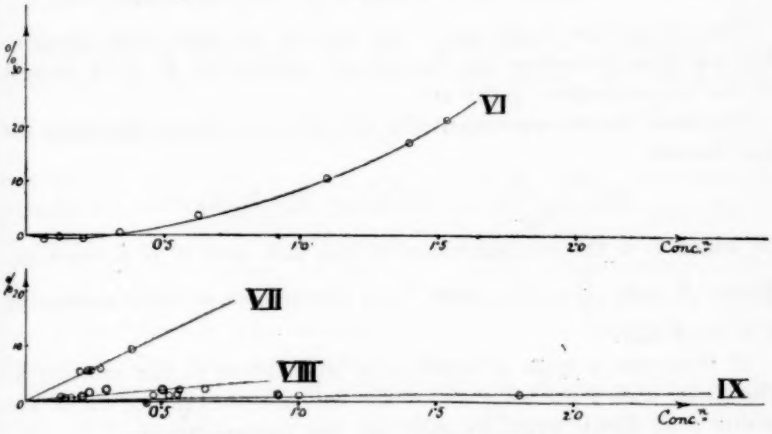
TABLE V. (Curve VI., Fig. 2). *Sodium Sulphate.*

HAc.	Salt.	R_1.	R_2.	R_1. (corr.).	R_2. (corr.).	$100\left[\frac{R_1 - R_2}{R_2}\right]$	Expts.
0·22	(0·07)	0·669	0·673	0·669	0·674	−0·7	5
0·22	(0·13)	0·674	0·673	0·673	0·674	−0·2	8
0·25	(0·22)	0·674	0·675	0·671	0·674	−0·4	7
0·25	(0·35)	0·683	0·675	0·678	0·674	+0·5	5
0·27	(0·61)	0·710	0·677	0·700	0·675	+3·8	2
0·29	1·10	0·762	0·678	0·743	0·675	+10·0	1
0·21	1·40	0·807	0·673	0·786	0·674	+16·6	1
0·22	1·54	0·839	0·673	0·813	0·674	+20·6	1

TABLE VI. (Curve VII., Fig. 2). *Lithium Chloride.*

0·2—0·22	0·2—0·25	0·7143	0·673	0·7116	0·674	5·57	3
0·2269	0·2799	0·7188	0·673	0·7147	0·674	6·00	1
0·2469	0·3930	0·7450	0·674	0·7375	0·674	9·40	1

FIG. 2.



VI. Na_2SO_4, *corr.* VIII. KNO_3, *corr.*
VII. LiCl „ IX. $NaCH_3{\cdot}CO_2$, *corr.*

Percentage increase in ratios of acetic acid in distillate and residue due to added salts.

TABLE VII. (Curve VIII., Fig. 2). *Potassium Nitrate.*

0·21	0·22	0·6944	0·673	0·6940	0·674	1·13	2
0·24	0·3—0·5	0·7198	0·674	0·7110	0·674	2·32	2

TABLE VIII. (Curve IX., Fig. 2). *Sodium Acetate.*

0·11	(0·14)	0·6822	0·667	0·6769	0·671	0·8	3
0·1—0·23	0·4—0·67	0·6948	0·671	0·6799	0·673	0·9	7
0·1—0·28	0·9—1·1	0·7001	0·673	0·6799	0·673	1·3	3
0·2900	1·810	0·7244	0·678	0·6834	0·675	1·3	1

The increase of R_1, the relative concentration of the distillate, for the same solution of acetic acid, that is, the expression

$100\left(\frac{R_1 - R_2}{R_2}\right)$ amounted to no less than 62 per cent. (observed) in the case of 2·3*N*-sodium chloride.

The increase for most salts seems proportional to the concentration of the salt and independent of the concentration of acetic acid.

Curves II—V of Fig. 1 and VI of Fig. 2 show this percentage increase plotted against the concentrations, and they point convincingly towards a straight line function between these two values. Sodium sulphate differs from all the other salts in that the experimental evidence shows a slightly negative effect at lower concentrations, up to about 0·3*N*.

Note on the Calculation of Residues in the Presence of Salts which exhibit a Straight Line Function of the Ratio Increase.

The calculation is similar to the one for the pure acid solution, but we must introduce the functional relation of R_1 with regard to the concentration of the salt.

We have found experimentally for all salts except the sulphate and acetate

$$100\left(\frac{R_1 - R_2}{R_2}\right) = 100K\rho \text{ or } R_1 = R_2(K\rho + 1),$$

in which ρ is the concentration of the salt and K is a constant. Hence $R_1 = R_2\left(\frac{K}{V} + 1\right)$, where V is the volume in litres containing 1 mol. of salt.

If there are y mols. of acetic acid in V litres of the solution in the flask, and a quantity dv of the solution containing dy of the acetic acid distils over, we may set the concentration of the distillate equal to $\frac{dy}{dV} = R_1\frac{y}{V} = R_2\left(\frac{K}{V} + 1\right)\frac{y}{V}$. Since $c = \frac{y}{V}$, and by differentiation $\frac{dc}{c} = \frac{dy}{y} - \frac{dV}{V}$, $\frac{dy}{dV} = c + V\frac{dc}{dV} = R_2\left(\frac{K}{V} + 1\right)c$, or $\frac{dc}{c} = \left(\frac{R_2K}{V^2}\ \frac{R_2 - 1}{V}\right)dV$.

Integrating,

$$ln\,\frac{c_0}{c_1} = R_2K\left(\frac{V_0 - V_1}{V_0 \cdot V_1}\right) + (R_2 - 1)ln\,\frac{V_0}{V_1},$$

or

$$\log\frac{C_1}{C_0} = \frac{1}{2{\cdot}303}\left[(1 - R_2)\left(\log\frac{V_0}{V_1}\right)2{\cdot}303 + R_2K\left\{\frac{V_1 - V_0}{V_1 \cdot V_0}\right\}\right],$$

where C_0 and C_1 are the concentrations and V_0 and V_1 the volumes in the distilling flask before and after distillation.

An alternative formula deducible in the same way is.

$$\log \frac{y_0}{y_1} = \frac{R_2}{2{\cdot}303}\left[2{\cdot}303 \log \frac{V_0}{V_1} - K\left\{\frac{V_0 - V_1}{V_0 \cdot V_1}\right\}\right].$$

Either of these expressions can be used to calculate the concentration of the acetic acid in the distilling flask if the initial value of the salt concentration and either its increase or the relative volume of the residual solution are given. They contain two constants. $100K$ is the one which is peculiar to the added salt, and it is simply the percentage increase by $1{\cdot}0N$-salt. The other, R_2, is the ratio of acetic acid in distillate and residue for the same solution in the absence of salt. It is convenient to express V_1 as a fraction of V_0, the volume at the beginning of the distillation containing 1 mol. of salt; but the initial concentration of salt in mols. per litre $= \frac{1}{V_0}$.

Inspection of the equations show that they are identical with that deduced above for solutions of pure acetic acid, except for the correcting factor $R_2K\left(\frac{V_0 - V_1}{V_0 \cdot V_1}\right)$. This factor, of course, disappears for large values of V_0, that is, for very low concentration of added salt. Conversely, for very high concentrations of salt it is predominant, as is evident from the consideration that for, say, $2{\cdot}6N$-potassium chloride, no separation takes place, owing to the concentration of acetic acid in the distillate having been so raised as to equal that of the residue. Above such concentrations, the residue becomes weaker instead of stronger.

The general behaviour of a distillation is shown graphically in curve VIA of Fig. 1, which assumes that $1{\cdot}0N$-sodium chloride was initially present ($V_0 = 1$). As the distillation proceeds, the salt accumulates, and the concentration of acetic acid in the residue slowly rises to a maximum where 50 per cent. of the liquid has distilled over ($V_1 = 0{\cdot}5$). At this point, $\log \frac{C_1}{C_0} = 0{\cdot}03$, whence the increase of concentration is 7·2 per cent. At $V_1 = 0{\cdot}27$, when 73 per cent. has been distilled over, the concentration of the acid is again the same as it was before the distillation. Beyond this point, the value for $\log \frac{C_1}{C_0}$ assumes rapidly negative values, owing to the high concentration of salt in the residue.

The general equation may be tested by one of our experimental results. Taking the last pair of values in table III for potassium chloride, $1{\cdot}0N$-potassium chloride increases the ratio of acetic acid by 18·5 per cent., hence $K = 0{\cdot}185$. Further, $R_2 = 0{\cdot}674$,

$V_1 = \frac{1{\cdot}128}{1{\cdot}953} V_0$, $V_0 = \frac{1}{1{\cdot}128}$. These values inserted in the equation lead to the prediction that $C_1 = 1{\cdot}078 C_0$. Experimentally, C_0 was $0{\cdot}2118N$ (less 1 per cent. for metathesis) and C_1 after distillation $0{\cdot}2194N$ (plus 5 per cent. for the three corrections). Hence $C_1 = \frac{0{\cdot}230}{0{\cdot}210} C_0 = 1{\cdot}095 C_0$. In general, the concentrations observed appear to agree with the predicted values within about 2 per cent.

To sum up, the process of concentration or separation of the constituents of a binary mixture by means of distillation may thus be considerably accelerated or retarded by the addition of a salt, and will largely depend on the values of the constants R_2 and K, that is, on the nature of the mixture and of the added salt.

(6) *Discussion of the Results.*

The remarkable effect of a salt on the partial vapour pressure of acetic acid must be evident from the preceding. Comparing the slopes of the various graphs showing the relationship between salt concentration and percentage ratio increase, it appears that the effect is greatest for the chlorides of lithium, sodium, and potassium, and least for sodium acetate. The effect is in all cases independent of the concentration of the acetic acid.

The increase of the concentration of the residue in the flask for acetic acid in aqueous solution during the distillation, not very rapid in itself, is still less if salt is also present. At a concentration of $2{\cdot}3N$-sodium chloride, the residue becomes weaker; in other words, the vapour phase in the flask contains more acetic acid than the liquid from which it originates.

For sodium sulphate up to about $0{\cdot}35N$, the experimental evidence for the ratio increase seems somewhat complicated. If anything, there is a negative effect, as the course of curve VI in Fig. 2 indicates. Beyond $0{\cdot}35N$, the effect is decidedly positive. Between $0{\cdot}35N$ and $1{\cdot}1N$, the graph is practically a straight line, but beyond $1{\cdot}1N$ its slope appears to increase until, at $1{\cdot}55N$, the limit of solubility is approached.

Sodium acetate up to $1{\cdot}8N$ shows only a very slight effect.

Although the effect of the cation is undeniable (note, for example, the greater slope of the ratio increase for sodium chloride as compared with the one for potassium chloride), the influence of the anion seems to be the predominating factor. The series sodium acetate, potassium nitrate, potassium thiocyanate, sodium sulphate, potassium chloride, lithium chloride, sodium chloride, shows the increase in a progressive degree. It is evident that this order is not that of the Hofmeister or lyotropic series.

It is well known that there is a general qualitative similarity between the effect of neutral salts on such various phenomena as solubilities of gases and non-electrolytes, surface tension, compressibility, maximum density of water, viscosity, dielectric constant, imbibition and gelatinisation of gels, and increase or decrease of rate of catalysis. The explanation of this undoubted parallelism is wholly unknown, and in each individual case there are pronounced exceptions. In the present instance, the exceptions are the acetate and the sulphate, although they may be paralleled by certain cases of catalysis. Possibly in the case of the sulphate our correction for metathesis (formation of HSO_4') has not been sufficiently great. The effects are reconcilable with a solvate form of the dissociation theory.

With regard to the main thesis of this paper, it has now been proved that the reactivity of the undissociated acetic acid is increased by addition of such salts as sodium chloride. A 0·2*N*-solution is affected to the extent of 5·5 per cent. by 0·2*N*-sodium chloride. It was pointed out in the earlier paper (*loc. cit.*) that Walpole's measurements of electromotive force for this particular case gave a result for the hydrogen ion which was 7 or 8 per cent. too high. These two effects, 5·5 and 7 or 8 per cent., are equal within the experimental error, and thus the effect on the dissociation constant deduced for acetic acid cancels out and leaves that constant unchanged by the presence of the salt.

Thus the electromotive force data may be regarded as agreeing with all the other data bearing on this subject, and the experimental evidence all points to the conclusion that the dissociation constants of weak substances are not appreciably affected by the addition of salts. One point we have not investigated, namely, the effect of salts on the chemical potential of the acetate ion.

Summary.

(1) It is shown experimentally that many salts enhance the partial vapour pressure of acetic acid in aqueous solution by very appreciable amounts. In the case of 2·3*N*-sodium chloride, the increase amounts to no less than 62 per cent.

(2) Since this partial pressure is a measure of the reactivity of the undissociated acid in the solution, the undissociated acid must be regarded as exhibiting enhanced chemical potential in the presence of such salts. This is parallel with the available data for the effect of such salts on the measurement of hydrogen ion by electromotive force. The enhancement is thus discovered to be operative on both sides of the chemical equation, and hence to leave the dissociation constant of acetic acid sensibly unaltered.

These experiments remove the only remaining evidence (apart from the ambiguous behaviour of certain insufficiently investigated colloids) for the view that salts might have been regarded as increasing the strength of weak acids.

(3) Whereas a number of salts increase the partial pressure of acetic acid to an extent proportional to the concentration, sodium sulphate exhibits a more complicated behaviour, whilst sodium acetate has only a very slight effect. All electromotive force data on weak acids in the presence of salts other than sodium acetate require to be corrected for the effects here described.

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CXXV.—*Some Ternary Systems containing Alkali Oxalates and Water.*

By ALBERT CHERBURY DAVID RIVETT and EDMUND ARTHUR O'CONNOR.

THERE has been considerable discussion at various times regarding the alleged formation of certain double oxalates of the alkali metals. Wenzel is quoted by some early writers as maintaining the existence of the double salts $K_2C_2O_4,Na_2C_2O_4$ and

$$K_2C_2O_4,(NH_4)_2C_2O_4,$$

but Rammelsberg (*Ann. Phys. Chem.*, 1850, [ii], **79**, 562) has thrown doubt on the one case and Souchay and Lenssen (*Annalen*, 1856, **99**, 31) on the other.

Foote and Andrew (*Amer. Chem. J.*, 1905, **34**, 164) drew the same conclusions as Rammelsberg and Souchay and Lenssen, and claimed to have shown that these double oxalates do not exist at 25° in the solid state. They state that the solid monohydrates of potassium and ammonium oxalates remain in equilibrium with a common saturated solution, and that the same holds for anhydrous sodium and hydrated potassium oxalates. A few years later, Barbier (*Bull. Soc. chim.*, 1908, [iv], **3**, 725) described a double oxalate of potassium and ammonium, stating that it might readily be formed by adding a concentrated solution of potassium oxalate to a saturated solution of ammonium carbonate. The analysis he quotes points to a pure, 1:1, anhydrous double salt.

None of the authors mentioned made complete investigations by the solubility method. Foote and Andrew (*loc. cit.*) obtained a few solubility figures, but to determine the solid phases present they relied on a general principle laid down in a previous paper (*ibid.*, p. 153) that when two salts are mixed in varying proportions and treated with water at a constant temperature, the residue of undissolved solid remains constant in composition and the solution varies if a pure double salt is present, whilst, on the other hand, the residue varies and the solution remains constant in composition when a mere mixture of the two single salts is present. This rule is liable to mislead, if only because it does not take into account the possibility of the formation of mixed crystals (solid solutions).

It has seemed worth while, therefore, to apply the solubility method more fully to some of these ternary systems of alkali oxalates in water. Knowledge of the solid phases present has been obtained by the customary graphic method of plotting in a triangular diagram the percentage compositions of pure solution and of the moist solid (or "residue") in equilibrium with it, and extrapolating the straight line joining the two points to the composition of the pure solid uncontaminated with adhering solution. The systems investigated are those containing potassium, sodium, and ammonium oxalates, in pairs, with water. The solid phases of the individual salts stable at these temperatures with their own aqueous solutions are, respectively, $K_2C_2O_4,H_2O$, $(NH_4)_2C_2O_4,H_2O$, and $Na_2C_2O_4$.

Experimental.

I. *System:* $K_2C_2O_4$–$(NH_4)_2C_2O_4$–H_2O *at* 25° *and* 50°.

The system potassium oxalate, ammonium oxalate, and water has been examined at 25° and 50°, and the figures obtained are given in tables I and II, respectively, and plotted in Fig. 1.

Suitable mixtures of the salts (monohydrates) and water were heated in bottles, which were sealed and placed in a thermostat, in which they were continuously rotated for about forty-eight hours. Undissolved solid was allowed to settle, and clear solution drawn into a pipette through a small plug of cotton wool held in rubber tubing. A known weight was diluted to a suitable volume for subsequent analyses. Residues were obtained by pouring solution and suspended solid on to a Buchner funnel, drawing the solution through rapidly by means of a pump, but disconnecting the pump before more than a very small amount of air had been

drawn through the moist solid. A slight loss of water vapour at 50° is inevitable, but with rapid working it can be made almost negligible.

Total oxalate was determined by titration of a fraction of the stock solution with standard potassium permanganate, ammonium by distillation with alkali and absorption of ammonia in standard acid, and potassium by difference. Concentrations have been expressed in percentages by weight, but as densities have been determined in all cases, figures for concentrations in other terms are readily obtainable.

TABLE I.

25°.

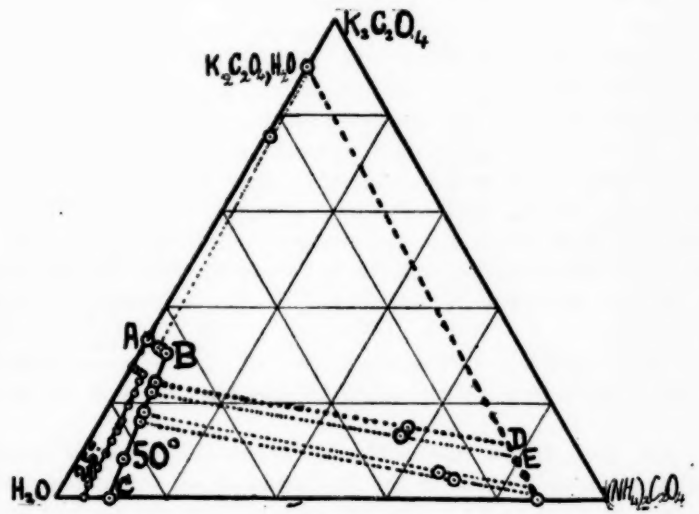
No.	Density.	Percentage composition of solution or residue (R). $K_2C_2O_4$.	$(NH_4)_2C_2O_4$.	H_2O.	Solid phases.
1	1·021	—	5·01	95·0	$(NH_4)_2C_2O_4,H_2O$.
2	1·040	2·67	4·72	92·6	Solid solution of $K_2C_2O_4,H_2O$ in $(NH_4)_2C_2O_4,H_2O$.
R 2	—	0·44	81·3	18·3	,,
3	1·058	4·32	4·48	91·2	,,
R 3	—	2·41	56·4	41·2	,,
4	1·068	6·51	4·38	89·1	,,
R 4	—	2·75	61·1	36·1	,,
5	1·087	9·48	4·16	86·4	,,
R 5	—	2·62	72·3	25·1	,,
6	1·107	12·10	4·01	83·9	,,
7	1·124	14·18	3·78	81·0	,,
8	1·128	15·37	3·68	80·9	,,
9	1·137	16·54	3·57	79·9	,,
R 9	—	2·14	80·4	17·2	,,
10	1·166	19·39	3·32	77·3	,,
R 10	—	4·37	76·4	19·2	,,
11	1·185	21·9	3·10	75·0	,,
R 11	—	6·70	76·2	19·2	,,
12	1·204	24·3	2·90	72·8	,,
R 12	—	13·4	61·9	24·7	,,
13	1·217	25·9	2·75	71·3	Two solid solutions: (i) $K_2C_2O_4,H_2O$ in $(NH_4)_2C_2O_4,H_2O$. (ii) $(NH_4)C_2O_4,H_2O$ in $K_2C_2O_4,H_2O$.
14	1·216	26·3	1·83	71·9	Solid solution of $(NH_4)C_2O_4,H_2O$ in $K_2C_2O_4,H_2O$.
15	1·216	26·8	0·85	72·3	,,
16	1·215	27·2	—	72·8	$K_2C_2O_4,H_2O$.

TABLE II.

50°.

No.	Density.	Percentage composition of solution or residue (R). $K_2C_2O_4$.	$(NH_4)_2C_2O_4$.	H_2O.	Solid phases.
1	1·034	—	9·63	90·4	$(NH_4)_2C_2O_4,H_2O$.
2	1·080	7·99	8·40	83·6	Solid solution of $K_2C_2O_4,H_2O$ in $(NH_4)_2C_2O_4,H_2O$.
3	1·136	16·20	7·10	76·7	,,
R 3	—	4·20	70·0	25·8	,,
4	1·154	17·99	6·79	75·2	,,
R 4	—	5·72	66·7	27·6	,,
5	1·187	22·4	6·10	71·5	,,
R 5	—	13·3	55·9	30·8	,,
6	1·203	24·4	5·75	69·8	,,
R 6	—	15·2	56·3	28·5	,,
7	1·254	30·4	4·78	64·8	Two solid solutions: (i) $K_2C_2O_4,H_2O$ in $(NH_4)_2C_2O_4,H_2O$. (ii) $(NH_4)_2C_2O_4,H_2O$ in $K_2C_2O_4,H_2O$.
8	1·251	31·0	3·34	65·7	Solid solution of $(NH_4)_2C_2O_4,H_2O$ in $K_2C_2O_4,H_2O$.
9	1·252	31·5	2·64	65·9	,,
R 9	—	75·5	0·47	24·0	,,
10	1·252	33·1	—	66·9	$K_2C_2O_4,H_2O$.

FIG. 1.



With the exception of some of the residues, these results are plotted in Fig. 1, and show distinctly that only two solubility

curves are obtainable at each of these temperatures, the two meeting sharply at a quadruple (or condensed triple) point.

There is no evidence at all of the existence of a double salt. On the other hand, it is quite apparent from the relations between compositions of solutions and corresponding residues (shown only for 50°) that the solid phase present in those complexes in which excess of ammonium oxalate is taken (curve *CB*) is not this pure solid, but contains in addition some potassium oxalate. The proportions of the two in the solid vary according to the composition of the solution in equilibrium, and the evidence is definite that mixed crystals of the two salts are produced. The more potassium oxalate there is in the solution, the more there is in the solid. The same must hold with regard to the solids in equilibrium along the curve *AB*. These solids will be mainly potassium oxalate with steadily increasing proportions of ammonium oxalate. The amounts of ammonium oxalate in solutions along this curve are, however, so small that a slight error in the analysis of the residue may make the extrapolation method uncertain in showing the solid phase.

Some of the mixed crystals were dried by draining on a porous tile in a closed vessel immersed in the thermostat. Analysis proved the two constituents of these mixed crystals to be the respective monohydrates.

The form of the isotherms, with a sharp change of direction at *B*, shows that two distinct solid phases must be present at this, a univariant, point. It follows that the series of mixed crystals is not complete, but that there is a limit to the solubility of each solid in the other. These limits have not been determined. The compositions are also not given by such points as *D* and *E* in Fig. 1, those of the exact solid solutions in equilibrium with the corresponding liquid solutions at the other ends of the tie-lines. Some of the crystals may have had a core of the pure main constituent, so that the mean composition represented by *D* and *E* may be low in potassium oxalate as compared with the solid solution itself. All that is established is the existence of mixed crystals.

The work of Foote and Andrew (*loc. cit.*) is not quite extended enough to show this. They obtained only the points *A*, *B*, and *C* at 25°.

It has been found impossible to repeat the work of Barbier (*loc. cit.*), which pointed to the formation of an anhydrous double salt, $K_2C_2O_4,(NH_4)_2C_2O_4$. By following closely the method which he described for isolating the compound, crystals were precipitated which, after drying on a porous tile, contained 81·1 per cent. of

ammonium oxalate, 5·8 per cent. of potassium oxalate, and (by difference) 13·1 per cent. of water. After washing with a solution of ammonia, as recommended by Barbier, the proportion of potassium oxalate decreased slightly. It appears certain that this precipitate consists of mixed crystals of the two hydrates.

It is of interest to note that Souchay and Lenssen (*loc. cit.*), following Wenzel's instructions for preparing the alleged double salt, obtained crystals which they stated to be ammonium oxalate, but containing 0·9 per cent. potash.

II. *System:* $Na_2C_2O_4$–$(NH_4)_2C_2O_4$–H_2O *at* 25° *and* 50°.

Sodium oxalate differs from both the potassium and ammonium salts in crystallising anhydrous from aqueous solution; hence it is less likely that mixed crystals will be formed between it and either of the other two. The figures in tables III and IV show that neither double salt nor mixed crystals occur in the sodium–ammonium system at 25° or 50°. The method of analysis was similar to that adopted for the previous system.

TABLE III.

25°.

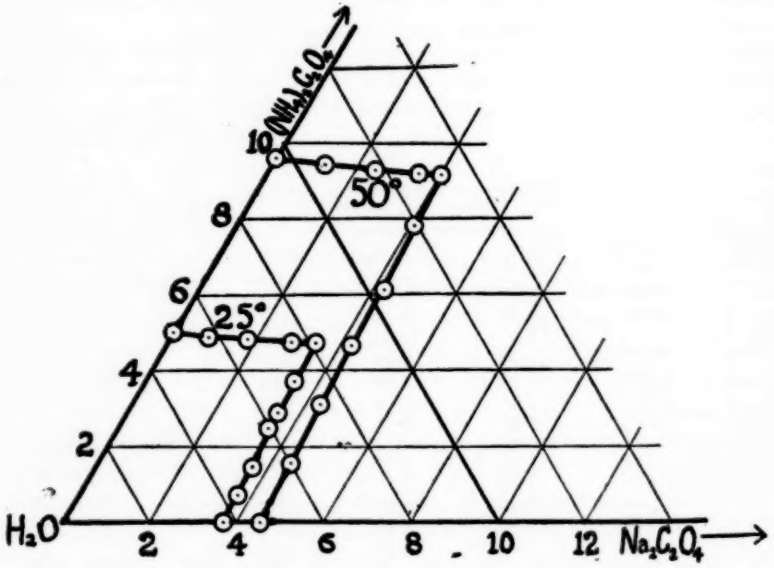
No.	Density.	Percentage composition of solution or residue (R). $Na_2C_2O_4$.	$(NH_4)_2C_2O_4$.	H_2O.	Solid phases.
1	1·027	3·73	—	96·3	$Na_2C_2O_4$.
2	1·030	3·69	0·74	95·6	
3	1·033	3·65	1·49	94·6	
R 3	—	63·9	0·53	35·6	,,
4	1·037	3·50	2·48	94·0	,,
5	1·039	3·51	2·89	93·6	,,
6	1·043	3·46	3·77	92·8	,,
7	1·047	3·41	4·74	91·8	,,
					$Na_2C_2O_4$ and $(NH_4)_2C_2O_4.H_2O$.
8	1·043	2·85	4·75	92·4	$(NH_4)_2C_2O_4.H_2O$.
9	1·035	1·82	4·81	93·4	
R 9	—	0·40	66·9	32·7	,,
10	1·028	0·89	4·88	94·2	,,
11	1·021	—	5·01	95·0	,,

TABLE IV.

50°.

No.	Density.	Percentage composition of solution or residue (R). $Na_2C_2O_4$.	$(NH_4)_2C_2O_4$.	H_2O.	Solid phases.
1	1·023	4·54	—	95·5	$Na_2C_2O_4$.
2	1·031	4·46	1·59	94·0	,,
3	1·036	4·37	3·14	92·5	,,
4	1·044	4·28	4·64	91·1	,,
R 4	—	70·0	1·47	28·5	,,
5	1·049	4·29	6·12	89·6	,,
6	1·056	4·13	7·86	88·0	,,
R 6	—	56·7	3·54	39·8	,,
7	1·063	4·05	9·19	86·8	$Na_2C_2O_4$ and $(NH_4)_2C_2O_4,H_2O$.
8	1·059	3·57	9·21	87·2	$(NH_4)_2C_2O_4,H_2O$.
R 8	—	1·47	63·4	35·1	,,
9	1·051	2·45	9·32	88·2	,,
10	1·042	1·25	9·46	89·3	,,
11	1·034	—	9·63	90·4	,,

FIG. 2.



The results are plotted in Fig. 2, where, on account of the sparing solubilities of the two components, only a single angle of the triangle is shown. The residues are omitted.

III. *System:* $K_2C_2O_4$–$Na_2C_2O_4$–H_2O *at* 25°.

Foote and Andrew (*loc. cit.*) concluded that anhydrous sodium oxalate and the monohydrate of potassium oxalate can exist side

by side in equilibrium with a common saturated solution, and the figures in table V, plotted in Fig. 3, confirm this, showing that neither double salts nor mixed crystals are formed. Solutions and residues were analysed by determining total oxalate by titration and total anhydrous salts by weighing after evaporation and drying at 125°, at which temperature potassium oxalate monohydrate is readily dehydrated. As the amount of sodium oxalate present is always relatively small, this indirect method is less accurate than that employed in the previous two cases.

FIG. 3.

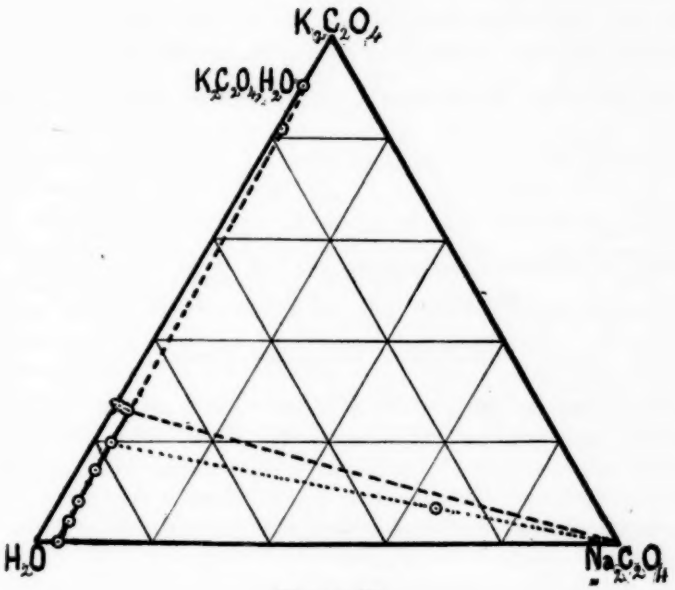


TABLE V.

25°.

No.	Density.	Percentage composition of solution or residue (R). $K_2C_2O_4$.	$Na_2C_2O_4$.	H_2O.	Solid phases.
1	1·215	27·2	—	72·8	$K_2C_2O_4,H_2O$.
2	1·218	26·8	0·77	72·4	,,
3	1·223	26·3	1·71	72·0	,,
4	1·226	26·2	2·17	71·6	,,
R 4	—	81·9	0·73	17·4	,,
5	1·228	26·1	2·50	71·4	$K_2C_2O_4,H_2O$ and $Na_2C_2O_4$.
6	1·178	19·6	3·21	77·2	$Na_2C_2O_4$.
R 6	—	7·00	65·3	27·7	,,
7	1·135	14·4	3·21	82·4	,,
8	1·084	8·10	3·40	88·5	,,
9	1·057	3·99	3·71	92·3	,,
10	1·026	—	3·71	96·3	,,

Summary.

(1) It has been stated by some authors and denied by others that potassium and ammonium oxalates form a double salt. Isotherms have been obtained at 25° and 50°, and show that at these temperatures mixed crystals of the monohydrates are formed.

(2) Anhydrous sodium oxalate has been shown to exist in equilibrium with ammonium oxalate monohydrate and a common, saturated solution at 25° and 50°. Neither double salts nor mixed crystals are formed.

(3) The same has been shown to be the case at 25° with anhydrous sodium oxalate and potassium oxalate monohydrate.

UNIVERSITY OF MELBOURNE. [*Received, November 1st*, 1919.]

CXXVI.—*The Decomposition of Carbamide in the Presence of Nitric Acid.*

By TUDOR WILLIAMS PRICE.

WHILE investigating the use of dilute nitric acid as a nitrating agent at elevated temperatures, it was found that nitration was entirely inhibited by the addition of carbamide, although all the acid was used up. This reaction was considered worthy of further investigation, the results of which are given in the present communication.

The action of concentrated nitric acid on carbamide nitrate in the solid state at the ordinary temperature has been studied by Franchimont (*Rec. trav. chim.*, 1884, **3**, 216), who found that a gas was given off slowly, consisting of equal parts of carbon dioxide and nitrous oxide. The volume of gas was such that it contained all the carbon of the carbamide as carbon dioxide, and half the nitrogen as nitrous oxide, the other half forming ammonium nitrate.

No account has been found in the literature of the action of dilute nitric acid on carbamide, although the action of hydrochloric acid and sulphuric acid has been studied by Fawsitt (*Zeitsch. physikal. Chem.*, 1902, **41**, 601) and of hydrochloric acid by Werner (T., 1918, **113**, 84).

Fawsitt (*loc. cit.*) found the reaction between carbamide and dilute hydrochloric and sulphuric acids to be unimolecular, which

he explained by the assumption that the former is first transformed to a small extent into ammonium cyanate at a measurable rate, and, if the inverse change is neglected, according to a unimolecular reaction. The ammonium cyanate is thereupon decomposed into the ammonium salt of the acid used, and carbon dioxide at a much greater rate than that at which ammonium cyanate is formed, and thus the decomposition of carbamide in the presence of hot acids is almost identical with the rate at which it is transformed into ammonium cyanate.

Werner (*loc. cit.*), on the other hand, states that the above assumption is quite unnecessary, and that the velocity of the reaction is regulated by the rate of dissociation of carbamide (at 100°) into ammonia and cyanic acid, when both products of dissociation are removed practically as fast as they are generated.

Whichever scheme of the mechanism of the reaction is correct, the final products are the same, namely, carbon dioxide and the ammonium salt of the acid used. If the action of hot dilute nitric acid on carbamide is the same as that of hydrochloric acid, the reaction should be unimolecular, and the products should be carbon dioxide and ammonium nitrate.

Veley (*Proc. Roy. Soc.*, 1892, **52**, 27) has shown that nitric acid decomposes slowly at high temperatures, forming nitrous acid, the weaker the acid the higher being the temperature required for decomposition; also, it is well known that carbamide decomposes nitrous acid very readily, forming carbon dioxide and nitrogen. Hence it is possible that the true explanation of the disappearance of nitric acid when heated with carbamide in solution is the alternate formation of nitrous acid from nitric acid, and decomposition of the nitrous acid by carbamide. In this case, nitrogen will be present in the evolved gas, as well as carbon dioxide.

There are thus three separate methods of decomposition of carbamide by nitric acid, the gaseous products in each case being different. An analysis of the gas produced will then be of extreme importance.

As will be seen in the experimental part, the reaction between carbamide and nitric acid is unimolecular, and the gas evolved consists entirely of carbon dioxide.

Experimental.

The carbamide used was ordinary commercially pure carbamide recrystallised four times from absolute alcohol. The nitric acid solutions were made from pure distilled nitric acid, and contained

only a trace of nitrous acid. A normal solution of carbamide is taken to be one containing half its molecular weight in grams in a litre of water; all the other solutions of carbamide were made up on this basis.

Ten c.c. of the mixed solutions of carbamide and nitric acid were placed in hard-glass test-tubes, which were then sealed and placed in water at the required temperature. After various periods of heating, the tubes were withdrawn, cooled, opened, and their contents titrated with standard sodium hydroxide solution, using methyl-orange as indicator.

The majority of the experiments were made at 100°, but the reaction between $N/2$-carbamide and $N/2$-nitric acid was studied at 70°, 80°, 90°, and 100°.

The influence of certain salts on the velocity of the reaction was also examined.

In order to obtain figures comparable with those of Fawsitt, the velocity-constants for a unimolecular reaction were calculated according to the equation

$$k = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2},$$

instead of the correct equation,

$$k = \frac{1}{t_2 - t_1} \log_e \frac{a - x_1}{a - x_2},$$

where a is the initial concentration of carbamide, x_1 the amount of carbamide decomposed in time t_1, and x_2 the amount decomposed in time t_2. In every case, t_1 was fixed at sixty minutes, so as to obviate the error due to the time taken for the tube to reach the desired temperature.

a, x_1, and x_2 were obtained from the titre of sodium hydroxide immediately after mixing the two solutions, and the titre after times t_1 and t_2.

In one case, the constants for a bimolecular and termolecular reaction were calculated.

Results.—The results of two experiments are given in detail, and all are summarised in table I. It will be noted that the velocity-constant tends to increase towards the end of an experiment, and this is much more marked with N- and $2N$-solution than with the more dilute ones.

Experiment 3. N-*Carbamide* + N-*Nitric Acid at* 100°. $a = 50{\cdot}40$.

Time in minutes.	$a - x$.	$k_1 \times 10^5$ (unimolecular).	$k_2 \times 10^6$ (bimolecular).	$k_3 \times 10^7$ (termolecular).
60	45·50	—	—	—
120	40·51	84	45	84
180	35·66	84	50	101
270	29·53	89	56	127
360	24·21	91	64	163
480	17·84	(97)	—	—
600	13·35	(98)	—	—
960	5·18	(105)	—	—
1500	1·21	(109)	—	—

Mean value $k \times 10^5 = 87$.

Experiment 5. N/2-*Carbamide* + N/2-*Nitric Acid at* 100°. $a = 25{\cdot}43$.

Time in minutes.	$a - x$.	$k \times 10^5$.
60	22·75	—
120	19·81	101
180	17·25	100
270	13·96	101
360	11·39	100
480	8·29	105
600	6·36	102
900	3·00	104
1200	1·42	107
1500	0·83	(169)

Mean value $k \times 10^5 = 102$.

TABLE I.

Showing Velocity-constants obtained in the Decomposition of Carbamide.

Concentration of reaction mixture.	Temperature.	Duration of expt. in minutes.	No. of observations.	Mean value of $k \times 10^5$.	Maximum variation of k from mean.
2*N*-Carbamide + 2*N*-HNO_3 ...	100°	420	7	73	2·0
2*N*- ,, + *N*-HNO_3 ...	100	270	6	105	4·0
N- ,, + *N*-HNO_3 ...	100	360	5	87	4·0
N/2- ,, + *N*-HNO_3 ...	100	1800	9	88	3·0
N/2- ,, + *N*/2-HNO_3 ...	100	1200	9	102	5·0
N/4- ,, + *N*/2-HNO_3 ...	100	600	5	108	2·0
N/4- ,, + *N*/4-HNO_3 ...	100	420	7	111	3·0
N/8- ,, + *N*/8-HNO_3 ...	100	420	6	116	6·0
N/16- ,, + *N*/16-HNO_3	100	360	7	133	8·0
N/2- ,, + *N*/2-HNO_3 ... + *N*/2-NH_4NO_3	100	1500	10	122	5·0
N/2- ,, + *N*/2-HNO_3 ... + *N*/2-KNO_3 ...	100	900	9	118	6·0
N/2- ,, + *N*/2-HNO_3 ... + *N*/2-NH_4Cl	100	420	5	118	3·0
N/2- ,, + *N*/2-HNO_3 ... + *N*/2-KCl	100	600	8	116	3·0
N/2- ,, + *N*/2-HNO_3 ...	89	1800	9	23·0	2·8
N/2- ,, + *N*/2-HNO_3 ...	80	2790	9	9·3	0·7
N/2- ,, + *N*/2-HNO_3 ...	70	9360	10	2·4	0·3

Experiment 17.—Twenty-five c.c. of *N*-carbamide and 25 c.c. of *N*-nitric acid were heated at 100° in a boiling tube fitted with a reflux condenser. A delivery tube connected the top of the condenser to a nitrometer. The total air space from the level of the liquid in the boiling tube to the nitrometer was 34 c.c. One hundred c.c. of gas were collected in the nitrometer and rejected. It was considered that by this time all the air had been swept out of the apparatus, and collection of the gas for analysis was commenced. Fifty c.c. of this gas were almost entirely absorbed by a piece of moist potassium hydroxide, only a minute bubble being left. The gas was thus composed entirely of carbon dioxide, and did not contain any nitrous oxide or nitrogen, the small residue being either air which had not been completely swept out of the apparatus, or nitrogen from the trace of nitrous acid present in the nitric acid.

The heating of the carbamide and nitric acid solution was continued for fifty hours, at the end of which the solution was evaporated to dryness. On analysis, the residue was found to consist of ammonium nitrate with a little unchanged carbamide.

Discussion of Results.

The results show that the reaction between carbamide and nitric acid in dilute solution is undoubtedly unimolecular. The products consist entirely of carbon dioxide and ammonium nitrate. Hence the reaction is analogous to the decomposition of carbamide by hydrochloric or sulphuric acid, and is not due to the preliminary decomposition of nitric acid into nitrous acid with subsequent decomposition of the latter by carbamide.

On comparing the results with those obtained by Fawsitt for hydrochloric acid in table II, it will be seen that at all dilutions the velocity of reaction is greater with nitric acid than with hydrochloric acid.

TABLE II.

Showing Comparison between Velocity of Reaction at 100° *of Carbamide with Nitric Acid and Hydrochloric Acid.*

Reaction mixture.			$k \times 10^5$.	
			HNO_3.	HCl.*
2*N*-Carbamide	+ 2*N*-acid	.....	73	—
N- „	+ *N*- „	.....	87	58
N/2- „	+ *N*/2- „	.....	107	77
N/4- „	+ *N*/4- „	.....	111	90
N/8- „	+ *N*/8- „	.....	116	101
N/16- „	+ *N*/16- „	.....	133	101

* Fawsitt's results.

The velocity of reaction diminishes regularly with an increase in the concentration of the nitric acid, and no maximum point was found such as Fawsitt found for hydrochloric acid (*loc. cit.*, p. 612). Fawsitt and Werner both state that only free carbamide is active. According to Werner, the equilibrium between carbamide and its nitrate can be represented as follows:

$$HN{:}C\begin{cases}NH_2\\O\end{cases} + HNO_3 \rightleftharpoons HN{:}C\begin{cases}NH_2,HNO_3\\OH\end{cases},$$

and the reaction between carbamide and nitric acid, on the analogy of the reaction between carbamide and hydrochloric acid, can be represented thus:

Phase 1. $HN{:}C\begin{cases}NH_2\\O\end{cases} + HNO_3 = NH_4NO_3 + (HNCO \rightleftharpoons HO{\cdot}CN).$

Phase 2. $(HNCO \rightleftharpoons HO{\cdot}CN) + H_2O + HNO_3 = NH_4NO_3 + CO_2.$

The diminution of the velocity with increase in concentration of the acid can thus be explained, since it is only "free" carbamide, and not carbamide "fixed" as its nitrate, which takes part in Phase 1 of the reaction.

Fawsitt found that the decomposition of carbamide in the presence of hydrochloric acid was retarded slightly by the addition of ammonium chloride, but was accelerated in the presence of sulphuric acid by the addition of ammonium sulphate. He also found that the decomposition of carbamide in the presence of water alone was accelerated by the addition of ammonium carbonate, sodium chloride, and potassium chloride, whilst ammonium chloride and ammonium hydrochloride had a decided retarding effect.

In the presence of nitric acid, the present author has found that ammonium nitrate, potassium nitrate, ammonium chloride, and potassium chloride all have a distinct accelerating effect on the decomposition of carbamide at $N/2$-concentration.

According to the dissociation theory of the decomposition of carbamide, the first action of heat on it is the production of ammonia and cyanic acid; in the presence of acids, this is followed by combination of ammonia with acid, forming an ammonium salt, and by hydrolysis of cyanic acid, forming an ammonium salt and carbon dioxide. The addition of the ammonium salt, or of any salt containing an ion common with the ammonium salt, to the reaction mixture, should therefore have a retarding effect on the velocity of decomposition. As shown by the experiments, this is not the case when carbamide is decomposed in the presence of nitric acid, and hence it would seem that the dissociation theory of

the decomposition of carbamide is not applicable in the presence of nitric acid.

The great influence of temperature on the velocity will be seen from table III.

TABLE III.

Showing Effect of Temperature on Velocity of Reaction between N/2-*Carbamide and* N/2-*Nitric Acid.*

Temperature.	$k \times 10^5$.
100°	102·0
89	23·0
80	9·3
70	2·4

Below 80°, the velocity of decomposition of carbamide is small, and at 30° to 40° would be negligible; hence the use of excess of carbamide for the removal of nitrous acid from a mixture of nitrous acid and nitric acid will not be accompanied by loss of nitric acid as such if the temperature is not allowed to rise above 40°.

In conclusion, the author's best thanks are due to Messrs. Nobel's Explosives Company, Limited, and to Mr. William Rintoul, Manager of the Research Section, for the facilities afforded for carrying out this work and for permission to publish the results.

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CXXVII.—*Studies in Catalysis. Part XII. Catalytic Criteria and the Radiation Hypothesis.*

By WILLIAM CUDMORE MCCULLAGH LEWIS.

THE criteria which have been suggested from time to time as applying to the phenomenon of catalysis are as follows (compare Rideal and Taylor, "Catalysis in Theory and Practice," Chap. 2):

(1) The chemical composition of the catalytic agents is unchanged on completion of the reaction process.

(2) Minimal amounts of a catalytic agent are adequate for the transformation of large quantities of the reacting substances.

(3) A catalyst does not affect the final state of equilibrium.

(4) A catalyst modifies the velocity of two inverse reactions to the same degree.

(5) A catalytic agent is incapable of starting a reaction; it can only modify the velocity of the reaction.

Criteria (1) and (2) are closely related, (2), in fact, being the corollary of (1). Both would be accepted at once provided secondary effects are excluded. To this extent they state a fact of experience, and indicate that catalysis is simply a special case of ordinary chemical reactivity.

Criteria (3) to (5), which form a group by themselves, are in a different category, as representing generalisations which may or may not be true. Criterion (4) is the corollary of (3), so that the group contains two distinct criteria. Considerable difference of opinion exists at the present time regarding the validity of these conclusions, according to the point of view adopted as the basis of criticism. It is of some interest, therefore, to examine criterion (3) or (4) and criterion (5) from the point of view of the radiation hypothesis of chemical reactivity.

We shall consider criterion (5) in the first place. On the radiation hypothesis, the possibility of a reaction occurring depends on the existence of radiation of a type or frequency absorbable by the reacting substance, the quantum of which radiation is sufficiently large to communicate the necessary critical increment to the molecule. In the case of thermal radiation, which is the kind of radiation envisaged in the quantum theory, theoretically all possible wave-lengths or frequencies are represented at any temperature. Consequently, the type of radiation necessary for any reaction is present in the space occupied by the matter, and therefore every reaction is correspondingly possible. This must include the so-called catalytic reactions as well as those to which this name is not applied. From this point of view, therefore, can we conclude that a catalyst does not initiate, but simply accelerates, a process which would occur, although under certain conditions infinitely slowly? This cannot be affirmed without qualification.

In the form in which criterion (5) is stated, it is evidently assumed that the same process *may* occur whether the catalyst be present or not, but this assumption is not necessarily true. It seems necessary to ascribe in certain cases, if not in all, a definite stoicheiometric molecular mechanism to a catalyst, just as one would to any other reactant, and consequently, by adding such a catalyst, a new process commences (the origin of which is the field of radiation) that happens to give rise to certain end-products, which, we believe, might be attained in the absence of the catalyst. The fact appears to be that criterion (5), as ordinarily stated, involves a false antithesis. From the point of view of the radia-

tion hypothesis, a catalyst may be said either to render a reaction possible by supplying the necessary matter, or it may merely accelerate, according to circumstances. In no case is it the fundamental initiator of a process. The rôle played by the catalyst may be conveniently illustrated by the catalytic effect of an acid in the inversion of sucrose or the hydrolysis of an ester. Prior to the addition of the acid, the reaction is possible, involving reaction between a molecule of sucrose or ester and either a molecule of water or its ions, probably the undissociated molecule. On addition of the catalysing acid, the hydrogen ion accelerates the process already begun by the hydrogen ions already present. The undissociated molecule of the acid may also accelerate the reaction, but in doing so it is almost certain that it produces an intermediate substance, which was not formed in its absence. In so far as the intermediate stage is concerned, the molecule of the acid has rendered a new intermediate process possible, although the final products are independent of the nature of this intermediate stage. The real source or origin of initiation of any reaction, on the radiation hypothesis, is the radiation itself. The material catalyst, if it acts simply as a transformer, hastens a reaction which radiation has already initiated. The catalyst may also act as a molecular reactant, giving rise, under the stimulus of radiation, to new intermediate products. The validity of conclusion (5) depends, therefore, on the particular view adopted regarding the mechanism of the process. It seems that two distinct modes of mechanism are possible, and are apparently realised in the well-known acid catalyses. On one mode, the catalyst simply accelerates; on the other, it renders a new mechanism possible from the material point of view.

Turning now to criterion (3) or (4), which possesses much greater practical significance, the radiation hypothesis leads to the conclusion that, as a general principle, criterion (3) or (4) is certainly not true.

Let us take the simplest possible case of reversible reaction, represented by

$$A \rightleftharpoons B.$$

The substance A is characterised by being capable of absorbing radiation of frequency ν_A, as a result of which it is transformed into B. The substance B is likewise capable of absorbing radiation of frequency ν_B, as a result of which the process is reversed. The heat evolved, Q, on passing from A to B, is then given by the expression

$$Q = Nh(\nu_B - \nu_A),$$

where N is the Avogadro number and Q is referred to one gram-molecule of A transformed.

Let us consider the special case in which $\nu_A = \nu_B$, or approximately so. In this case, Q is zero, or approximately so. A catalyst acting as a transformer will in this case be unable to distinguish between the two types of molecules A and B, since each is capable of absorbing the same type, or approximately the same type of radiation. It will therefore catalyse both the direct and the reverse reaction equally. That is, the opposing velocity constants will be equally increased, and the equilibrium constant will remain unaffected by the presence of the catalyst. This result is in harmony with the criterion.

If, on the other hand, the heat of the process is considerable, that is, ν_A differs considerably from ν_B, then it no longer follows that a positive catalyst will equally accelerate both reactions. In general, it would not be expected to do so, and consequently, in general, the equilibrium point will be affected by the catalyst. It is a significant fact, in view of the conclusion just drawn, that those reactions, such as esterification or hydrolysis, in which the equilibrium point is not sensibly affected by the catalyst, are precisely those in which the heat effect is small.

In the above case we have been considering mainly homogeneous catalysis by means of ions. Let us now take the case of catalysis by the undissociated molecule, such as the molecule of hydrochloric acid, which is generally regarded as functioning through the formation of an intermediate ternary compound. Thus, Falk and Nelson (*J. Amer. Chem. Soc.*, 1915, **37**, 1732) represent the intermediate oxonium complex in the case of hydrolysis of esters as (ester,HCl,H_2O). In the reverse process, the corresponding compound is (carboxylic acid,HCl,alcohol). These two compounds are tautomeric, and may be identical. If they are identical, as Falk and Nelson assume, then the hydrochloric acid molecule will equally affect the direct and the reverse process, and thus leave the equilibrium point unchanged. This explanation of the mechanism of the effect produced by the undissociated molecule of the catalysing acid has certainly the advantage of simplicity. It has this implication, however. Such additive compounds are generally formed rapidly compared with the rate of any further decomposition which they may undergo. If this is so, and if the same intermediate compound is formed in the hydrolysis as in the esterification, it would follow that the velocity constants should be the same, and the equilibrium constant should therefore be unity. This is not in agreement with experiment, although it is significant that the value of K is not greatly removed from unity. Thus, experiment has shown that

$$K = \frac{[\text{methyl acetate}] \times [\text{water}]}{[\text{methyl alcohol}] \times [\text{acetic acid}]} = 4{\cdot}6$$

(compare Part V of this series of papers, T., 1916, **109**, 71).

This ratio means that the velocity constant of esterification is 4·6 times the velocity constant of hydrolysis. On the radiation view, this ratio is mainly determined by the relative value of the exponential terms, that is, by

$$e^{-Nh\nu_1/RT} \Big/ e^{-Nh\nu_2/RT},$$

where $Nh\nu_1$ is the critical increment of esterification and $Nh\nu_2$ is the critical increment of hydrolysis, that is,

$$e^{Nh(\nu_2-\nu_1)/RT} = 4{\cdot}6.$$

At 300° absolute we find, therefore, that $\nu_2 - \nu_1 = 1 \times 10^{13}$. Both ν_1 and ν_2 do not, however, lie very far from the value 2×10^{14}, so that the difference in respect of position of absorption of infra-red radiation is extremely small, being of the order of one-twentieth of the absolute value of either frequency. The same idea is conveyed by saying that the heat effect does not exceed 1000 calories. The fact, therefore, that the equilibrium constant possesses a value not unity, but not far removed therefrom, means on the radiation basis that the intermediate compounds are not identical, but tautomeric, and, further, that both kinds of molecule absorb almost the same frequency, so that any change in the equilibrium constant introduced by altering the concentration of the catalyst is insensible. (It may be noted that the relatively large change in K observed by Lapworth has its origin, as Lapworth has shown, in what is virtually a distinct reaction not directly connected with the actual esterification–hydrolysis process itself.) In the case considered we conclude, therefore, that as a practical guide the criterion (3) or (4) is true, that is, in those cases in which the equilibrium constant is not far removed from unity. The conclusion is obviously comparable with that drawn in connexion with ion catalysis.

In addition to homogeneous catalysis by dissolved substances in a given solvent, it is well known that different solvents themselves exert their own catalytic effect. From the point of view of radiation, we conclude that in this type of catalysis criterion (3) or (4) cannot, in general, be even approximately true, since each solvent is characterised by its own electromagnetic properties, that is, by its power of absorption at different wave-lengths, which differs from solvent to solvent, and consequently entails a different distribution of radiation density. The particular type of radiation required by the reactant is therefore present to a different extent, according to the nature of the solvent, and consequently the

velocity constant and equilibrium constant is a function of the solvent. Specific differences are further introduced by the mutual interaction of solvent and solute, whereby the effective frequency itself is altered to a slight extent.

Finally, as regards heterogeneous catalysis, evidence has been collected and presented by Bancroft (*J. Physical Chem.*, 1917, **21**, 573; 1918, **22**, 433) to show that the catalyst affects the equilibrium point of the process. Heterogeneous catalysis has been examined in a preliminary manner from the point of view of radiation (T., 1919, **115**, 182), and it is concluded that the equilibrium point must be a function of the nature and extent of the catalytic material, owing to the alteration in the values of the critical increments which is introduced by the presence of the catalyst. The catalytic layer here considered is only one molecule, or possibly two molecules, in thickness, that is, it is of the order 10^{-8} cm. In this layer, the final amounts of reactants and resultants will differ, in general, from the true equilibrium amounts characteristic of the homogeneous gas phase, for in the adsorption layer the relative amounts are determined by the relative adsorption capacities. If this is a complete statement of the phenomenon, it is evident that criterion (3) or (4) is inapplicable. There is, however, a further possibility to be considered.

The adsorbed reactants and resultants are in an activated condition as long as they are actually in the adsorption layer. In time, they necessarily pass out into the homogeneous gas phase, owing to desorption. If these molecules at the moment of leaving the adsorption layer lose the extra energy which they possess and become immediately transformed into molecules of normal energy content, it follows that their relative concentration in the homogeneous gas phase becomes identical with that in the adsorption layer, for, in general, the reaction in the homogeneous phase is extremely slow. There is the possibility, however, that the activated reactants and resultants on leaving the true adsorption layer do not immediately revert to the inactive state, but may retain their activity for a short space corresponding, perhaps, with a layer 10^{-6} cm. in thickness. If this is the case, there will be a rapid chemical change in this *extra*-adsorption layer, which will tend to bring the concentrations of the reactants and resultants into the ratio required by the law of mass action for the homogeneous phase. Whether the true equilibrium point would be attained or not would depend on the average life of the activated molecules. At moderately high temperatures, the average molecular velocity may be taken to be 10^5 cm. per second; hence it would require 10^{-11} second for a molecule to traverse a distance

of 10^{-6} cm. It is possible that the activated state may be maintained for a longer period of time than this, and therefore the more likely is the process to attain the true equilibrium position. The more selective the nature of the adsorption material, the further, in general, will the "equilibrium" of the adsorption layer depart from the true mass action equilibrium. Hence, even if such a compensating effect as that suggested above actually operates, criterion (3) or (4) cannot be regarded as valid.

It is concluded, therefore, that criterion (3) or (4) is, in general, not true; in homogeneous systems it approximates more closely to experiment the smaller the heat effect accompanying the reaction; in heterogeneous systems it is not certain whether even this approximation to validity holds good.

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CXXVIII.—*Criteria of the Degree of Purity of Commercial Toluene.*

By JOHN SCOTT LUMSDEN.

THE following investigation was undertaken for the Explosives Department of the Ministry of Munitions for the purpose of finding some easily applied method for estimating the degree of purity of commercial toluene, and is published with the permission of the Department.

Commercial toluene contains varying amounts of a liquid which cannot be nitrated and has distilled along with the toluene during rectification. This liquid has not been isolated, but in the following tests the assumption is made that it may be represented by a paraffin mixture which boils close to the boiling point of toluene. By fractionation of petrol, a quantity of such a liquid was obtained boiling at 108—112°.

Estimation of Toluene by Specific Gravity.—Pure toluene at 15° was found to have D 0·8712; the paraffin mixture had D 0·743. Since there is no change in volume on mixing toluene and paraffin, a graph was prepared to show the density of mixtures. From this graph, it was found that the presence of 1 per cent. of paraffin produced a lowering of the density of 0·0013.

Whilst such a graph may not be depended on to give the accurate

percentage of impurity present, because the toluene may be moist and the impurity may not be like that assumed, it is certainly useful in indicating poor samples. For example, of two samples of commercial toluene, (*a*) had D 0·872 and (*b*) 0·8613. Both were fractionated, with the following results: Sample (*a*) showed a trace of moisture, then boiled steadily at 110°. All fractions, right to the end, had D 0·8716. This was therefore a very good sample of toluene. Sample (*b*) showed a little moisture, and then boiled half a degree below, slowly rising to half a degree above 110°. The fractions had D 0·8623, 0·8621, 0·8622, 0·8619, 0·8612, 0·8586, and 0·8570. The original low density and the decreasing density of the fractions pointed to a considerable admixture of paraffins; from the graph, the indication is 7·7 per cent.

Estimation of Toluene by Nitration.—To effect nitration, potassium nitrate and sulphuric acid were employed, as described later. It was soon found that the nitration of toluene cannot be made to stop when the mononitro-compound is formed, but that any excess of acid is used up, producing the dinitro-compound; it was, however, proved, as the result of many experiments, that nitration stops quantitatively when all the toluene has been converted into the dinitro-compound.

Using nitration as a means of estimating toluene, there are obviously two methods which may be adopted, namely, by nitrating with a weighed excess of potassium nitrate, and determining the weight of nitric acid remaining after nitration, the amount of acid used is obtained, and from that the weight of toluene nitrated, or by isolating and weighing the dinitro-compound. Adopting the first method, it was found that the residual acid could be satisfactorily determined by the nitrometer, but that by the second method the dinitro-compound could not be completely recovered, because a small but definite amount remains in solution in the acid liquid from which the substance is filtered.

The nitration process is as follows. A 100 c.c. flask is weighed, and into this is weighed accurately, by dropping from a fine pipette, 2 grams of the sample to be nitrated. Five grams of pure dry powdered potassium nitrate are weighed in a watch-glass or aluminium scoop, and transferred with great care to the flask. The flask is cooled in water, and 30 c.c. of pure concentrated sulphuric acid are poured in rapidly, the flask being shaken continuously to prevent the formation of solid lumps, which, if formed, take some time to dissolve. When the action is over, a pale yellow, homogeneous liquid is obtained.

To cause the dinitro-compound to separate, about 60 c.c. of water are added, the first few c.c. being dropped in slowly, lest

the heat evolved should volatilise any nitric acid, and at the same time the flask is cooled in water.

The solid is obtained in soft flakes which are nearly white, and when the contents of the flask are quite cold, the separation may be considered complete. Filtration is effected by the aid of the pump, using a small porcelain funnel with a small filter paper; the preparation flask is washed out with several small amounts of water, which are poured through the funnel, and the solid is washed free of acid. The filtrate is transferred to a graduated cylinder, and, together with the washings of the filter flask, is made up to exactly 150 c.c.

The whole operation of nitration proceeds smoothly, and the only point where care is needed is when adding water to the nitrated liquid, great precautions being then necessary to avoid rise of temperature.

Calculations:

$$\underset{92}{C_6H_5\cdot CH_3} + \underset{202\cdot2}{2KNO_3} = \underset{182\cdot0}{C_6H_3(NO_3)_2\cdot CH_3}.$$

$$\underset{2}{\quad} \qquad \underset{4\cdot3956}{\quad} \qquad \underset{3\cdot95}{\quad}$$

(*a*) Two grams of toluene require for nitration 4·39 grams of potassium nitrate. One per cent. of this—0·0439 gram—remaining unused, represents 1 per cent. of impurity in the toluene. 0·004522 Gram of potassium nitrate gives 1 c.c. of gas in the nitrometer; 0·0439 gram therefore represents 9·72 c.c. Working with 2 grams of toluene, 9·72 c.c. of gas in the nitrometer at *N.T.P.* represent 1 per cent. of impurity.

(*b*) Five grams of potassium nitrate are used to nitrate 2 grams of toluene, but only 4·3956 grams are required. This is an excess of 0·6044 gram, which in the nitrometer would give 133·65 c.c. of gas.

(*c*) Two grams of toluene give 3·95 grams of dinitrotoluene. One per cent. of this—0·0395 gram—as a deficit in the yield, represents 1 per cent. of impurity in the toluene.

Examples of Nitration. (a) *Estimation by Nitrometer.*—Two grams of toluene were nitrated with 5 grams of potassium nitrate. The liquid was made up to 150 c.c., and 15 c.c. were taken for the nitrometer estimation. (The 15 c.c. were measured from a small burette into the cup of the nitrometer, and 10 c.c. of pure sulphuric acid were used to liberate the gas.) 19·8 C.c. of gas at 16° were obtained, or 18·71 at *N.T.P.* For the whole 150 c.c. this was 187·1 c.c.; deducting the known excess used, namely, 133·65 c.c., leaves 53·45 c.c. As 9·72 c.c. represent 1 per cent. of impurity, 53·45 c.c. represent 5·5 per cent. of impurity.

The following are the results of other estimations:

Pure toluene.	Good toluene.	Poor toluene.
150 c.c. liquid, 15 c.c. taken.	175 c.c. liquid, 20 c.c. taken.	150 c.c. liquid, 15 c.c. taken.
13·27 c.c. gas at N.T.P.	15·7 c.c. gas at N.T.P.	18·64 c.c. gas at N.T.P
For 150 c.c. liquid, 132·7 c.c.	For 175 c.c. liquid, 137·37 c.c.	For 150 c.c. liquid, 186·4 c.c.
From excess taken 133·6	From excess 133·65	From excess 133·6
−0·9 c.c.	3·72 c.c.	52·8 c.c.
− 0·9/9·72 = − 0·1 per cent.	3·72/9·72 = 0·38 per cent.	52·8/9·72 = 5·4 per cent.
Toluene 100·1 per cent.	Toluene 100 − 0·38 = 99·62 per cent.	Toluene 100 − 5·4 = 94·6 per cent.

The sample of pure toluene shows more than 100 per cent.; this is due to experimental loss. It will be realised that if the potassium nitrate is not pure and dry, or if there is any loss before the filtrate is made up to a definite volume, less nitric acid is found, and this is indicated as a small increase in the percentage of toluene.

(b) *Estimation by Weighing the Solid.*—The solid dinitro-compound is transferred from the filter funnel to a watch-glass and set in a desiccator over sulphuric acid, or the watch-glass may be set over a beaker of boiling water, when the solid melts to a clear liquid with water beneath it. On cooling, the solid forms a firm mass, from which water is readily removed by filter paper; then, after a much shorter time in the desiccator, the weight becomes constant.

It was found that when the volume, after nitration, was made up to 150 c.c., approximately 0·11 gram of solid remained in solution, and this amount is added to the weight found in the following examples.

Two grams of "pure" toluene gave 3·8337 grams of solid; adding 0·11 gram, the total dinitro-compound was 3·9437 grams; 100 per cent. toluene should give 3·9564 grams, therefore the deficit is 0·0127 gram. 0·0395 Gram deficit represents 1 per cent. of impurity, and 0·0127 gram 0·32 per cent. The toluene was therefore 100 − 0·32 = 99·68 per cent.

Two grams of a poor sample of toluene gave a deficit of 0·2573 gram, that is, 0·2573/0·0395 = 6·5 per cent. The toluene was therefore 100 − 6·5 = 93·5 per cent.

Estimation of Toluene by Miscibility with Acetic Acid.

Whilst engaged on this investigation, a report by Professor Orton was received describing the experimental work detailed in his recent paper (this vol., p. 1055). He there showed that when

88 to 90 per cent. acetic acid is mixed with toluene in the proportions of 1 c.c. of acid to 0·8 c.c. of toluene, two layers are formed, and on raising the temperature, a point of complete miscibility is reached which is definite for the same strength of acid, and so sharply defined that it can be read to one-tenth of a degree. He showed also that the temperature of miscibility of toluene rises regularly with the dilution of the acetic acid, and further, that for a given strength of acid the temperature of miscibility of toluene containing paraffin rises in direct proportion to the amount of paraffin present.

Working with two strengths of acetic acid, 87·9 and 89·5 per cent., and using pipettes of certain volumes, he prepared curves from which the percentage of a mixture of toluene and paraffin could be found when the temperature of miscibility with one of these acids had been determined. The method is susceptible of great accuracy, but it is very troublesome to prepare acetic acid of a definite strength, and almost impossible to keep a concentrated acid without absorption of moisture from the air, and, moreover, it requires so much care to carry out the process as set down by Professor Orton that it could scarcely be used as a commercial test. The following modification, consisting in the changing of an absolute to a comparative method, may, however, be carried out in any commercial laboratory.

A quantity of concentrated acetic acid of unknown strength is taken, and with equal volumes of this, the temperatures of miscibility with equal volumes of pure toluene, toluene with 5 per cent. of paraffins, and the sample of toluene to be tested, are found. Then, since the percentage of paraffins is proportional to the increase in the temperature of miscibility, the comparison of the rise of temperature of miscibility of the sample with that of the 5 per cent. paraffin mixture gives the paraffin content of the sample.

To carry out the test, there is required:

(1) A quantity of pure toluene, which need not be synthetically pure, but might be considered as 100 per cent. quality.

(2) A mixture of this toluene with 5 per cent. of paraffins, made by mixing 95 grams of toluene with 5 grams of paraffins of the same boiling point, prepared by the distillation of petrol.

(3) Acetic acid, prepared by taking 100 grams of glacial acetic acid, adding a few c.c. of water, and, by trial with toluene in the proportions described below, finding if two layers are formed and if the temperature of miscibility is somewhere between 25° and 30°.

(4) The sample to be tested.

The proportions of acetic acid and toluene found by Professor

Orton as suitable for the test may be adhered to, and two pipettes prepared, one delivering 1 c.c. and the other 0·8 c.c., or quantities in these proportions, but they need not be exact. The pipettes are made from narrow glass tubing, and must have fine capillary points to deliver very slowly. A test-tube 1·2 cm. in diameter serves as a vessel in which the miscibility point is determined, and while the test is being made it may for convenience be fixed to the thermometer by a rubber band. The test is carried out as follows. With the larger pipette, acetic acid is run into the test-tube, and pure toluene is added from the smaller pipette. The tube is then fixed to the thermometer, which must be graduated in tenths of a degree. Water is heated in a beaker holding about 2 litres, the temperature being raised speedily, and by stirring with the thermometer and tube, an approximation to the miscibility point is found by noting the temperature when the two layers disappear and a homogeneous liquid is obtained.

A little cold water is then added to the beaker, the flame is turned very low, the water thoroughly stirred, and as the temperature slowly rises, the thermometer and tube are moved continuously in the water. As the miscibility point is approached, the two layers disappear, the liquid becomes opalescent, and then suddenly becomes transparent. This is the point at which the temperature is noted. By cooling the water in the beaker 1°, the test may be repeated.

The same procedure is gone through with the 95 per cent. toluene and with the sample being examined, the tube being washed out thoroughly each time and dried in an air-oven. The following are results obtained:

	Pure toluene.	95 Per cent. toluene.	Sample.
(1) The miscibility temperature was	32·0°	38·3°	41·4°
(2) Same sample on another day, the acid being different	33·4	40·3	44·0

From (1) 38·3° − 32° = 6·3°, and 41·4° − 32° = 9·4°. A rise of 6·3° represents 5 per cent. of impurity, 9·4° represents 7·4 per cent.

From (2) 40·3° − 33·4° = 6·9°, and 44·0° − 33·4° = 10·6°. A rise of 6·9° represents 5 per cent. of impurity, 10·6° represents 7·6 per cent.

It is seen that the strength of the acid does not require to be known: it has only to remain constant during the time that three portions are withdrawn, and the pipettes do not require to be of any definite volume, although they must deliver precisely the same volume each time.

The three tests might be carried out simultaneously by having three test-tubes attached to the thermometer, one with each mixture,

and the three points of miscibility determined as the temperature of the water is raised.

When the same sample of toluene was tested by the different methods, the following results were obtained:

From specific gravity curve	92·3 per cent.
From nitrometer estimation after nitration	92·9 ,,
By weighing dinitro-compound	92·6 ,,
By temperature of miscibility with acetic acid	92·5 ,,

Conclusions.—The specific gravity of commercial toluene gives a fair indication of the amount of impurity present; the estimation of the temperature of miscibility with acetic acid is quickly done, and, although a comparative method, if skilfully carried out is trustworthy; the nitration and estimation of the excess of nitric acid by the nitrometer is believed to be the most accurate test and indicates the total nitration which has taken place, and the weighing of the solid after nitration gives the actual practical yield of nitro-compound.

By none of the methods, under ordinary conditions of working, can an accuracy closer than one-half per cent. be expected.

THE TECHNICAL COLLEGE,
DUNDEE.

[*Received, October 16th,* 1919.]

CXXIX.—1:3-*Benzodiazolearsinic Acids and their Reduction Products.*

By ROBERT REGINALD BAXTER and ROBERT GEORGE FARGHER.

SINCE the discovery of salvarsan (Ehrlich and Bertheim, *Ber.*, 1912, **45**, 756), many attempts have been made to prepare derivatives or closely allied products which would render unnecessary the somewhat elaborate technique involved in the clinical use of the original compound, which, owing to its pronounced acidity, has to be converted into the disodium salt, in turn alkaline in reaction, before use. Neosalvarsan, the sodium *N*-methylenesulphinate of salvarsan, introduced to avoid these difficulties, possesses many advantages, such as ready solubility and neutral reaction, but, in spite of these, there is a consensus of opinion in favour of salvarsan, as its spirochæticidal action appears to be stronger and more certain.

In this and in other cases the attempts have led to the formation of acid derivatives giving neutral salts with alkalis. The authors desired, on the other hand, to obtain hydrochlorides soluble in water and sufficiently less acid in reaction than salvarsan to admit

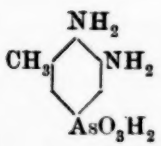
of their direct use, and it was with this object in view that the present investigation was commenced, since it was considered probable that the hydrochlorides of the arsenobenzenes derived from 1:3-benzodiazole (benzoglyoxaline) would fulfil these requirements. Further, considering the properties of the glyoxaline nucleus, they might be expected to exert acidic as well as basic properties, and thus closely resemble salvarsan itself.

Additional interest would attach to such compounds in view of their relationship to 3:4:5:3′:4′:5′-hexa-aminoarsenobenzene and its *N*-methyl derivatives (D.R.-P. 286667, 286668, 286854, 286855, 294276; E.P. 7488 and 8041 of 1913; U.S.P. 1081079; Benda, *Ber.*, 1914, **47**, 1316; Karrer, *Ber.*, 1916, **49**, 1448), which are stated to possess the unexpected property of dissolving in alkali hydrogen carbonates, forming carbamates with the same degree of alkalinity as that of normal blood serum and a relatively low toxicity (D.R.-P. 269660; E.P. 1667 of 1914).

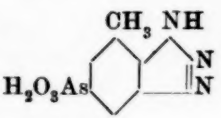
So far as the authors are aware, the benzodiazolearsinic acids have not been examined, Bertheim (*Ber.*, 1911, **44**, 3092), who described 3:4-diaminophenylarsinic acid and several of its derivatives, making no mention of them. They are, however, readily obtained by the well-known reaction of ortho-diamines with formic or acetic acid, whereby the acyl derivative first formed suffers loss of a molecule of water if a monoacyl, or of a molecule of acid if a diacyl derivative, with consequent closing of the ring (compare Ladenburg, *Ber.*, 1875, **8**, 677; Wundt, *Ber.*, 1878, **11**, 826).

The comparative stability of 3:4-*diacetylaminophenylarsinic acid*, which crystallises from boiling water unchanged, and does not alter save for slight decomposition when heated at 250°/20 mm., and, generally, the stability of diacyl-*o*-diamines (compare Bistrzycki and Ulffers, *Ber.*, 1890, **23**, 1876), seems to indicate that in the absence of anhydrides the reaction proceeds with intermediate formation of a monoacyl derivative.

5:6-*Diamino*-m-*tolylarsinic acid* (I), which, together with 3:4-diaminophenylarsinic acid (Bertheim, *loc. cit.*), formed the starting material for the investigation, was obtained by the reduction of 5-nitro-6-amino-*m*-tolylarsinic acid (this vol., p. 989) with sodium hyposulphite. It undergoes all the condensations typical of an



(I.)



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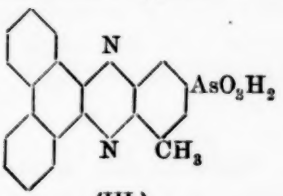
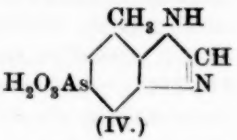


(III.)

o-diamine, giving, for example, with sodium nitrite in acid solution, 7-*methyl*-1:2:3-*benzotriazole*-5-*arsinic acid* (II), and with phenanthraquinone, 4-*methylphenanthraphenazine*-2-*arsinic acid* (III). The latter derivative shows the colour reactions characteristic of phenanthraphenazine.

With boiling glacial formic acid, the acids readily yielded 7-*methyl*-1:3-*benzodiazole*-5-*arsinic acid* (IV) and 1:3-*benzodiazole*-5-*arsinic acid* (V) respectively.



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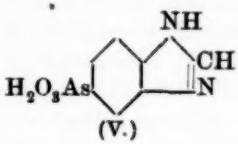
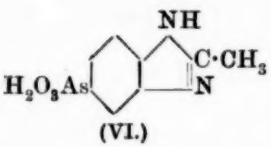
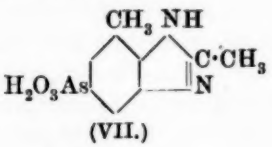


(V.)

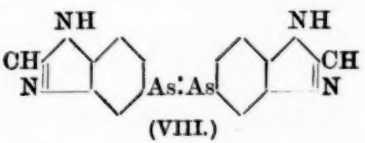
The action of acetic acid did not proceed quite so smoothly. 3:4-Diaminophenylarsinic acid, although stated (Bertheim, *loc. cit.*) to be readily soluble in acetic acid, is far from being so, and, on boiling with acetic acid, acetic anhydride, or a mixture of the two, gives rise to very highly coloured products, which are difficult to purify. If the reaction is carried out as described in the experimental portion of this paper, the main product is 3:4-*diacetylaminophenylarsinic acid*, which, on heating with water in a sealed tube at 130°, yields 2-*methyl*-1:3-*benzodiazole*-5-*arsinic acid* (VI). In the case of the higher homologue, the desired reaction takes place predominantly, with the formation of 2:7-*dimethyl*-1:3-*benzodiazole*-5-*arsinic acid* (VII). Incidentally, it may be mentioned that it has since been found that if 3:4-diaminophenylarsinic acid, dissolved in the requisite amount of sodium hydroxide (40 per cent. solution) to form the monosodium salt, is treated with sufficient acetic anhydride to neutralise the sodium hydroxide and form acetic acid with the water present, and then boiled, the main product of the reaction is the benzodiazole derivative.



(VI.)



(VII.)



(VIII.)

The reduction of the above acids with hypophosphorous acid, although it proceeds normally, leads to gelatinous products difficult

to handle, and consequently the reduction was carried out by means of sodium hyposulphite. This gives pale yellow *arsenobenzenes*, insoluble in water, which were converted into hydrochlorides by precipitating their solutions in acetic acid with excess of hydrochloric acid, or by treating the suspensions of the bases in water with just sufficient hydrochloric acid to bring about solution, and precipitating as before. The *hydrochlorides* form pale yellow powders, soluble in water, but very sparingly so in the usual organic solvents. Their aqueous solutions react strongly acid to litmus, but neutral to methyl-orange.

It was expected that this acidity would prove too great for purposes of intravenous injection, and that it would be difficult to distinguish between the effect due to the acidity and that due to the arsenic compound. This was confirmed by experiments with 5:5′-*arseno*-1:3:1′:3′-*benzodiazole* (VIII) by Miss Soref, of the Wellcome Physiological Research Laboratories.

Experimental.

3:4-*Diaminophenylarsinic Acid.*

The preparation of considerable quantities of this acid was carried out according to the directions given by Bertheim (*loc. cit.*), save that it was found advisable to omit the boiling of the solution after the reduction with sodium hyposulphite, as this diminished the yield and gave a more highly coloured product.

1:3-*Benzodiazole*-5-*arsinic Acid* (V).

Ten grams of 3:4-diaminophenylarsinic acid were boiled under a reflux condenser for six hours with 100 c.c. of glacial formic acid. After removal of the excess of formic acid by distillation, water was added, when 7·5 grams of crystalline material rapidly separated. To remove adhering traces of colouring matter, the product was treated with charcoal in dilute alkaline solution. On making neutral to methyl-orange, crystallisation commenced at once, practically the whole being recovered in a pure state.

1:3-*Benzodiazole*-5-*arsinic acid* crystallises from water, in which it is sparingly soluble, in clusters of minute, flattened prisms, which are anhydrous. On heating, it gradually darkens above 250° and decomposes rapidly about 297° (corr.).

Found: N = 11·4; As = 30·8.

$C_7H_7O_3N_2As$ (242·1) requires N = 11·6; As = 30·96 per cent.

5:5′-*Arseno*-1:3:1′:3′-*benzodiazole* (VIII).

A solution of 5 grams of 1:3-benzodiazole-5-arsinic acid in 100 c.c. of water containing 1·2 grams of sodium hydroxide was treated with 50 grams of sodium hyposulphite and 11·5 grams of magnesium chloride dissolved in 300 c.c. of water, and the mixture heated, with stirring, at 60° for two hours in an atmosphere of carbon dioxide, by which time the precipitation of the yellow arsenobenzene was complete. After cooling, the product was collected, well washed with water, suspended in 90 c.c. of water, dissolved by the addition of sufficient hydrochloric acid to form the dihydrochloride, filtered from traces of undissolved matter, and precipitated by pouring into an equal volume of concentrated hydrochloric acid. The hydrochloride was collected, well washed with alcohol and ether, and dried in a vacuum over sulphuric acid. The yield amounted to 3·9 grams.

5:5′-*Arseno*-1:3:1′:3′-*benzodiazole* is obtained as a bright yellow powder practically insoluble in water or the usual organic solvents, sparingly, if at all, soluble in methyl alcohol containing hydrochloric acid, but fairly readily so in 50 per cent. acetic acid. The *dihydrochloride* forms a pale yellow powder soluble in water, very sparingly so in methyl alcohol or ethyl alcohol, and quite insoluble in acetone or ether. The aqueous solution reacts acid to litmus, but neutral to methyl-orange. After drying in a vacuum overnight, it retains solvent equivalent to two molecules of water.

Found: N = 11·3; As = 30·2; Cl = 13·8.

$C_{14}H_{10}N_4As_2,2HCl,2H_2O$ (493·1) requires N = 11·4; As = 30·4; Cl = 14·4 per cent.

3:4-*Diacetylaminophenylarsinic Acid and* 2-*Methyl*-1:3-*benzodiazole*-5-*arsinic Acid* (VI).

Experiments in which diaminophenylarsinic acid was heated with glacial acetic acid, with acetic anhydride, with acetyl chloride and pyridine, or with acetic anhydride in the presence of a trace of sulphuric acid, were unsuccessful, owing to the considerable amount of decomposition which occurred. It was found, however, that if the acid, dissolved in methyl alcohol, was treated with a mixture of acetic acid and acetic anhydride, and the methyl alcohol then removed as completely as possible by distillation on the water-bath, the resulting solution, after heating to active boiling for four hours, gave an excellent yield of a product, which, from its composition, proved to be the diacetyl derivative of diaminophenylarsinic acid.

3:4-*Diacetylaminophenylarsinic acid* crystallises from water, in

which it is fairly readily soluble, as a felted mass of fine needles which retain from 2 to 2·5 per cent. of solvent.

Found: loss at 110° (two specimens) 2·6, 2·2.

In dried material: N = 8·8; As = 23·8.

$C_{10}H_{13}O_5N_2As$ (316·1) requires N = 8·9; As = 23·7 per cent.

As the product did not lose acetic acid when heated to 250°/20 mm., it was heated with ten times its weight of water in a sealed tube for four hours at 130°, when the desired reaction took place almost completely.

2-*Methyl*-1:3-*benzodiazole*-5-*arsinic acid* crystallises from water, in which it is somewhat sparingly soluble, in minute needles containing two and a-half molecules of water of crystallisation, the last half molecule being removed with difficulty at 110°, but fairly readily at 120°. After drying at 110°, it darkens on heating above 250° and decomposes at about 270° (corr.).

Found: loss at 110° = 15·5.

$C_8H_9O_3N_2As,2\frac{1}{2}H_2O$ requires H_2O = 15·0 per cent.

In dried material: C = 37·3; H = 3·8; N = 10·7; As = 29·3.

$C_8H_9O_3N_2As$ (256·1) requires C = 37·5; H = 3·5; N = 10·9; As = 29·3 per cent.

2:2′-*Dimethyl*-5:5′-*arseno*-1:3:1′:3′-*benzodiazole*.

This was prepared in the same manner as 5:5′-arseno-1:3:1′:3′-benzodiazole, which it resembles very closely in its properties.

The *dihydrochloride* forms a pale yellow powder, soluble in water, but almost completely insoluble in methyl alcohol, ethyl alcohol, ether, or acetone. After drying in a vacuum for twenty-four hours, it retains solvent approximating to three molecules of water. In aqueous solution it reacts acid to litmus but neutral to methyl-orange.

Found: N = 10·3; Cl = 12·7; As = 28·0.

$C_{16}H_{14}N_4As_2,2HCl,3H_2O$ (539·1) requires N = 10·4; Cl = 13·1; As = 27·8 per cent.

5:6-*Diamino*-m-*tolylarsinic Acid* (I).

A solution of 8·6 grams of 5-nitro-6-amino-*m*-tolylarsinic acid in 75 c.c. of water and 6·2 c.c. of 10*N*-sodium hydroxide was cooled to −1° and treated, in one operation, while stirring vigorously, with 20·4 grams of sodium hyposulphite. When the reaction was complete, as shown by the change in colour, the solution was filtered, treated with 8·1 c.c. of hydrochloric acid (D 1·12), and the resulting acid, which separated in the course of a few minutes,

collected, washed with water, and recrystallised from water, in which it is sparingly soluble in the cold, but fairly readily so on warming. It separates in colourless needles, which contain between one and a-half and two molecules of water of crystallisation. It dissolves fairly readily in methyl alcohol or acetic acid, but is very sparingly soluble in ether, benzene, or petroleum. Its solution in dilute hydrochloric acid gives a characteristic, deep violet coloration with a drop of a dilute solution of potassium dichromate. It appears to decompose slowly on keeping.

Loss at 110° = 11·2.

$C_7H_{11}O_3N_2As,1\frac{1}{2}H_2O$ requires 9·9 per cent.

$C_7H_{11}O_3N_2As,2H_2O$ requires 12·8 per cent.

In dried material: N = 11·3; As = 30·4.

$C_7H_{11}O_3N_2As$ (246·1) requires N = 11·4; As = 30·5 per cent.

7-Methyl-1:2:3-*benzotriazole*-5-*arsinic acid* (II) was obtained by treating a solution of 3:4-diamino-*m*-tolylarsinic acid in dilute hydrochloric acid with a molecular proportion of sodium nitrite. It forms a crystalline powder very sparingly soluble in water, but more readily so in alcohol. It crystallises from 50 per cent. alcohol in minute, colourless, glistening needles, which are anhydrous, and gradually decompose on heating above 280°.

Found: N = 16·6.

$C_7H_8O_3N_3As$ (257·1) requires N = 16·4 per cent.

4-Methylphenanthraphenazine-2-arsinic acid (III) was obtained by the condensation of molecular proportions of phenanthraquinone and 3:4-diamino-*m*-tolylarsinic acid in acetic acid solution. It forms an amorphous, yellow powder, sparingly soluble in water and the usual organic solvents. With concentrated sulphuric acid, it develops an eosin-red colour, with nitric acid a cherry-red, and with hydrochloric acid an insoluble red compound. The colour is discharged in all three cases by dilution with water. It dissolves in dilute sodium carbonate or sodium hydroxide, but a flocculent precipitate of the sodium salt is thrown down on the addition of excess of the reagent.

Found: N = 6·4.

$C_{21}H_{15}O_3N_2As$ (418·2) requires N = 6·7 per cent.

7-Methyl-1:3-*benzodiazole*-5-*arsinic Acid* (IV).

Two grams of 3:4-diamino-*m*-tolylarsinic acid were boiled with 20 c.c. of glacial formic acid for six hours. The isolation of the product was carried out as in the case of 1:3-benzodiazole-5-arsinic acid, save that the treatment with charcoal was found to be more

effective in acid solution. The air-dried product contains only traces of moisture and resembles the lower homologue very closely in its properties. It dissolves sparingly in water and crystallises in minute, prismatic needles, which darken when heated above 280° and melt and decompose at about 300° (corr.).

Found: loss at 110° = 1·3.

In dried material: N = 10·8; As = 29·4.

$C_8H_9O_3N_2As$ (256·1) requires N = 10·9; As = 29·3 per cent.

7 : 7′-Dimethyl-5 : 5′-arseno-1 : 3 : 1′ : 3′-benzodiazole.

This was obtained by the reduction of the above acid with sodium hyposulphite in the manner previously described (p. **1376**), as a pale yellow powder, insoluble in water and the usual organic solvents, but moderately soluble in acetic acid. The corresponding *dihydrochloride* forms a pale yellow, granular powder soluble in water, but insoluble in methyl alcohol, ethyl alcohol, ether, or acetone. After drying for twenty-four hours under greatly reduced pressure, it retained solvent corresponding with two molecules of water.

Found: N = 10·6; As = 28·6; Cl = 13·1.

$C_{16}H_{14}N_4As_2,2HCl,2H_2O$ (521·1) requires N = 10·75; As = 28·8; Cl = 13·6 per cent.

2 : 7-Dimethyl-1 : 3-benzodiazole-5-arsinic Acid (VII).

This acid was obtained by the prolonged action (six to eight hours) of boiling acetic acid on 5 : 6-diamino-*m*-tolylarsinic acid, the isolation being carried out in the usual manner. It is somewhat soluble in boiling water, but sparingly so in cold, and separates from the former in minute, prismatic needles which contain two molecules of water of crystallisation.

Found: loss at 110° = 12·2.

$C_9H_{11}O_3N_2As,2H_2O$ requires 11·8 per cent.

In dried material: N = 10·6; As = 27·9, 27·5.

$C_9H_{11}O_3N_2As$ (270·1) requires N = 10·4; As = 27·75 per cent.

2 : 7 : 2′ : 7′-Tetramethyl-5 : 5′-arseno-1 : 3 : 1′ : 3′-benzodiazole.

The above acid was readily reduced to the corresponding arsenobenzene by sodium hyposulphite, under the conditions previously employed. The *arsenobenzene* closely resembles those already described in its physical and chemical properties. The *dihydrochloride* forms a pale yellow powder soluble in water, but insoluble

in the usual organic solvents. After drying for twenty-four hours in a vacuum, it retains solvent corresponding with approximately two molecules of water.

Found: N = 10·0; As = 27·3; Cl = 12·3.

$C_{18}H_{18}N_4As_2,2HCl,2H_2O$ (549·1) requires N = 10·2; As = 27·3; Cl = 12·9 per cent.

WELLCOME CHEMICAL RESEARCH LABORATORIES,
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CXXX.—*The Equilibrium between Carbon, Hydrogen, and Methane.*

By HUBERT FRANK COWARD and STANLEY PIERCE WILSON.

EQUILIBRIUM in the system $C + 2H_2 = CH_4$ is more suited to experimental study, in one respect, than the more commonly investigated high-temperature dissociations, such as those of water, carbon dioxide, and hydrogen chloride. The proportion of methane in equilibrium with carbon and hydrogen diminishes with increasing temperature, and hence when equilibrium is once established in the zone of reaction, the cooling of the gaseous mixture on its removal from the carbon is not accompanied by an alteration in composition. It is a simple matter to ensure the absence of elementary carbon from any but the zone of measured temperature in which the equilibrium is attained.

The synthesis of methane from its elements was achieved by Bone and Jerdan (T., 1897, **71**, 41; 1901, **79**, 1042), who found that when a stream of hydrogen was passed over carbon at about 1200°, the resulting gaseous mixture was hydrogen containing, roughly, 1 per cent. of methane and no other hydrocarbon. This synthesis was confirmed by Bone and Coward (T., 1910, **97**, 1219), who obtained an almost theoretical yield of methane from 0·0824 gram of carbon.

The decomposition of methane into carbon and hydrogen, without the permanent formation of any detectable amount of any other hydrocarbon, was demonstrated by Bone and Coward (T., 1908, **93**, 1197).

The above-mentioned experiments, the forerunners of those now to be described, indicated that the equilibrium mixture at 1000—1200° contained, roughly, 1 per cent. of methane.

The determination of equilibrium values in the system has been

attacked in two other quarters. Mayer and Altmayer (*Ber.*, 1907, **40**, 2134) carried out experiments with the aid of a catalyst at temperatures ranging from 475° to 625°, and declared that Bone and Jerdan's methane formed at 1200° could not have arisen by the direct union of carbon and hydrogen. Pring (T., 1910, **97**, 498) found that a carbon rod lightly coated with platinum gave the value 0·55 per cent. of methane in equilibrium at 1200° and 0·30 per cent. at 1500°. Finally, Pring and Fairlie (T., 1912, **101**, 91) conducted experiments under high pressures, and, assuming the law of mass action to hold down to atmospheric pressure, calculated the following equilibrium values:

	Amorphous carbon.	Graphite.
1200°	0·36 per cent. of methane	0·24 per cent. of methane
1500°	0·21 „ „	0·07 „ „

The series of experiments, the results of which are recorded below, were conducted in essentially the same way as those described in detail by Bone and Coward (*loc. cit.*), except that the gaseous products of reaction were passed backwards and forwards over the carbon used until analysis showed the attainment of constancy of composition. The porcelain tube used to contain the reacting substances was, as before, set up coaxially with a wider one, through which dry hydrogen was passed. The wider tube was heated electrically by means of a platinum wire resistance. The temperature of the inner tube was, at 1100°, constant, within ±6°, for a length of 10 to 15 cm. (in different furnaces), which was ample to contain the carbon used. The latter was held in a quartz boat or in an open quartz tube just narrow enough to pass freely into the porcelain tube.

The temperature of the reaction zone was measured by means of a platinum and platinum–rhodium thermo-junction lying in the inner porcelain tube, but encased in a thin quartz tube; one wire was insulated from the other by running it through a fine quartz tube. The thermo-couple was standardised by means of lithium chloride (m. p. 605°), antimony (m. p. 628°), an alloy of 80 per cent. of copper and 20 per cent. of tin (m. p. 738°), potassium carbonate (m. p. 835°), and electrolytic copper (m. p. 1084°).

The gaseous products were collected direct from the furnace over a mixture of glycerol and water, and before being re-passed into the furnace were dried by passage through a U-tube containing fragments of dry stick potassium hydroxide.

The electrolytic hydrogen and the carbon were prepared as described by Bone and Coward. The methane was obtained by interaction between aluminium carbide and water, washed with

ammoniacal cuprous chloride and sulphuric acid, and collected after air had been displaced from the apparatus used for the preparation. Hydrogen was then removed by liquefaction of the gas by means of liquid air, and subsequent distillation. This procedure was proved to afford a satisfactory means for removing hydrogen from large volumes of methane. It cannot, however, be recommended for removing air from methane; methane must be prepared free from air in the first place unless large quantities of the gas are sacrificed during the fractional distillation after liquefaction.

Experiments at 1100°.

Synthesis of Methane.—Pure dry hydrogen was passed over 1 gram of carbon (ash, 0·06 per cent.) at the rate of about 1 litre per hour until from 5 to 6 litres of gas had been collected. A litre of this was measured and treated with palladium foil; the resulting concentrate was measured and analysed. The residual 4 to 5 litres of the gas, once passed over carbon, were re-passed at the same rate as before, and a sample was taken for analysis after concentration. The residual gas was then passed twice again over the heated carbon, and again sampled for analysis. The results of the analysis, calculated back to the unconcentrated mixtures, are (in percentages):

	1st passage.	2nd passage.	3rd passage.
Carbon monoxide	0·07	0·16	0·51
Methane	0·46	0·70	0·65
Nitrogen	0·21	0·51	0·67

The experiment was repeated with the same sample of carbon:

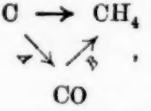
	1st passage.	2nd passage.	3rd passage.	4th passage.
Carbon monoxide	0·13	0·23	0·32	0·47
Methane	0·43	0·68	0·64	0·67
Nitrogen	0·26	0·49	0·56	0·69

Each experiment shows an accumulation of methane during the first and second passage of the gas over the carbon, but thenceforth the methane content remained practically constant.

The nitrogen content is a measure of the leaking in of air during the experiment and analysis, and in itself is unimportant. The carbon monoxide, due in part to air and in part to a slight oxidising action by the glaze of the heated tube, raises the question as to whether carbon monoxide may play some important part in the synthesis. It is just conceivable, although contrary to the results of other investigations,* that carbon monoxide would be

* Bone and Coward (T., 1908, **93**, 1987) showed that when a mixture of 98 per cent. of hydrogen and 2 per cent. of carbon monoxide was passed through a porcelain tube at 1100° in the absence of carbon, no more than 0·03 per cent. of methane was present in the issuing gas.

reduced by the large excess of hydrogen present to methane and water; the latter would regenerate carbon monoxide by reaction with carbon. If carbon monoxide acted as a catalyst in the synthesis, then the two reactions—whatever they might be precisely—indicated as *A* and *B* in the scheme



would each be fast in comparison with the rate of the direct synthesis. Hence the accumulation of carbon monoxide exhibited in the experiments would only be possible provided that the reversion of methane to carbon and hydrogen were a very rapid reaction indeed when the methane was increased above about 0·7 per cent. That this is not the case is shown by experiments (below) on the decomposition of methane at 1100°. The carbon monoxide is therefore produced as a side reaction between carbon and water vapour, and plays no part in the formation of at least the great proportion of the methane found.

Decomposition of Methane.—A mixture containing 2·0 per cent. of methane and 98·0 per cent. of hydrogen was passed over the same sample of carbon, eight times in all. The gas was sampled from time to time for analysis as before. The results were (in percentage):

	2nd passage.	5th passage.	8th passage.
Carbon monoxide	0·45	0·65	0·92
Methane	1·18	0·64	0·61
Nitrogen	0·49	0·52	1·04

Here, again, the steady formation of carbon monoxide is evident, whilst the methane-content becomes constant at or before the fifth passage, and shows the attainment of equilibrium, as in the synthetic experiments.

Synthesis and Decomposition of Methane in the Presence of Nickel.—One gram of the pure carbon was intimately mixed with 1 gram of nickel oxide, obtained by igniting the nitrate, and the mixture heated to 300° in hydrogen until no more water vapour was formed, and then raised gradually to 1100° in a current of hydrogen. The gas issuing from the tube was collected and repassed three times; analysis showed it to contain: carbon monoxide = 1·29, methane = 0·61, nitrogen = 0·49 per cent.

The decomposition of methane was conducted with a mixture containing 5·7 per cent. of methane and 94·3 per cent. of hydrogen. After five passages over the same mixture of carbon and nickel, the gas contained: carbon monoxide = 1·27, methane = 0·57, nitrogen =

1·33 per cent. The increase in carbon monoxide is ascribed to the well-known difficulty of reducing finely divided nickel oxide completely in hydrogen.

Collection of Results at 1100°.—The equilibrium values indicated above are:

	Pure carbon.	Carbon–Nickel mixture.
Synthesis	(i) 0·65; (ii) 0·67	0·61
Decomposition	0·61	0·57

The mean value for the equilibrium amount of methane at 1100° is therefore 0·62 per cent.

Experiments at 1000°.

Synthesis of Methane.—The synthesis of methane from the highly purified carbon used in the experiments at 1100° proved to be too slow for the attainment of equilibrium at 1000°. A less pure sample containing 0·5 per cent. of incombustible matter (silica) gave the following percentage results in an experiment conducted in a similar manner to the corresponding experiment at 1100°.

	1st passage.	2nd passage.	3rd passage.	4th passage.
Carbon monoxide	0·05	0·10	0·17	0·28
Methane	1·06	0·97	0·96	1·06
Nitrogen	0·15	0·44	0·32	0·31

Equilibrium is evidently established from the first. The carbon monoxide-content is much lower than in the experiments at 1100°, and although increasing throughout, has no appreciable influence on the methane-content of the gases. The high value for nitrogen in the second experiment is most probably due to a small in-leakage of air during the concentration of the sample of gas analysed.

An experiment with 1 gram of carbon containing 4 per cent. of platinum, finely disseminated, gave similar values:

	1st passage.	2nd passage.
Carbon monoxide	0·07	0·16
Methane	1·09	1·08
Nitrogen	0·09	0·19

Decomposition of Methane.—A mixture containing 2·0 per cent. of methane and 98·0 per cent. of hydrogen gave in two separate experiments:

	First experiment.		Second experiment.
	3rd passage.	5th passage.	2nd passage.
Carbon monoxide	0·19	0·41	0·55
Methane	1·16	1·13	1·06
Nitrogen	0·83	0·84	0·69

Synthesis and Decomposition of Methane in Presence of Nickel.—The same sample of a carbon–nickel mixture as was used for the experiments at 1100° gave the following results at 1000°. Starting with pure hydrogen, samples of the unconcentrated gases showed on analysis an approximately constant content of methane from the second to the sixth passages. The methane then present was determined accurately after concentration of the mixture: carbon monoxide = 2·2, methane = 1·23, nitrogen = 0·7 per cent. The decomposition of a 3·7 per cent. methane mixture gave, in similar circumstances, a constant content of methane from the third to the seventh passage. The final composition was: carbon monoxide = 1·1, methane = 1·18, nitrogen = 1·2 per cent.

Collection of Results at 1000°.—The equilibrium values indicated above are:

	Carbon (0·5 per cent. of ash).	Carbon–4 per cent. of platinum.	Carbon–Nickel.
Synthesis	1·01	1·09	1·23
Decomposition	1·13; 1·06	—	1·18

The mean value for the equilibrium amount of methane at 1000° is therefore 1·12 per cent.

Experiments at 850°.

The reaction between carbon and hydrogen proved to be too slow at 850° for equilibrium to be reached at that temperature within a reasonable period of time in the apparatus employed. Experiments with the nickel–carbon mixture were more successful. Synthetic experiments with a slow stream of gas showed that from the sixth to the eighteenth passage the methane content remained constant, according to the approximate results of analyses of unconcentrated samples of the mixture. The methane present at the end of the eighteenth passage was determined after concentration: carbon monoxide = 0·5, methane = 2·60, nitrogen = 1·3 per cent. Corresponding experiments on the decomposition of methane, carried out with a very slow stream of gas, showed constant composition between the second and fifth passages of the gas: carbon monoxide = 0·2, methane = 2·4, nitrogen = 0·6 per cent.

The equilibrium amount of methane at 850° is therefore 2·5 per cent.

Experiments at 650°.

Hydrogen and methane were separately heated for prolonged periods in contact with carbon at 650°. In no case did the analyses of the resulting mixtures indicate that equilibrium could be attained within any reasonable period of time, although attempts

were made to activate the carbon by means of finely divided nickel, (*a*) by grinding together nickel oxide and pure carbon and reducing in hydrogen at 300°; (*b*) by igniting a mixture obtained by evaporating nickel nitrate in the presence of excess of finely divided carbon, and heating finally in hydrogen at 300°; (*c*) by absorbing nickel nitrate in small pieces of porous porcelain, igniting, and depositing carbon by the prolonged passage of methane over the heated solid.

It is not concluded that it is impossible to prepare carbon in a sufficiently active state to attain equilibrium at this temperature, but the claim of Mayer and Altmayer (*loc. cit.*) to have succeeded at still lower temperatures is much weakened by the fact that they record no attempt to discover whether their gaseous products contained carbon monoxide. If, as it seems fair to assume, therefore, they overlooked carbon monoxide, much of their so-called methane may have had no actual existence. That there must have been carbon monoxide present in their products can scarcely be doubted in view of, first, the presence of large amounts of nitrogen, and, secondly, their use of somewhat large amounts of nickel, which, as is known, is difficult to obtain free from nickel oxide by reduction of the latter at a low temperature.

Summary and Conclusions.

The percentage composition of the equilibrium mixtures of methane and hydrogen in contact with amorphous carbon at atmospheric pressure is

	1100°.	1000°.	850°.
Methane	0·6	1·1	2·5
Hydrogen	99·4	98·9	97·5

These values will doubtless be capable of correlation by means of a thermodynamical equation, when the specific heats of the three reacting substances are known, together with the heat of formation of methane. Information as to the specific heat of methane at high temperatures is, however, wanting at present, and the heat of combustion of methane has apparently not been determined with a gas of sufficient purity. Calculation of the mean value of the latter between 850° and 1100° from the experimental values for the equilibrium, by means of the integrated form of the equation

$$\frac{d\log K}{dT} = -\frac{Q}{RT^2},$$

gives the value 18,000 calories, with a possible error of perhaps a couple of thousand calories.

In conclusion, the authors wish to acknowledge their indebtedness to assistance from the Government Grant Committee of the Royal Society, to Messrs. Johnson, Matthey and Co. for the loan of palladium, and to Mr. T. R. Bradbury, M.Sc., for valuable co-operation during one period of the work.

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CXXXI.—*The Properties of Ammonium Nitrate. Part I. The Freezing Point and Transition-temperatures.*

By REGINALD GEORGE EARLY and THOMAS MARTIN LOWRY.

AMMONIUM nitrate is remarkable amongst salts both for its easy fusibility and for the fact that the salt exists in not fewer than five crystalline forms, the ranges of stability of which are marked by a series of four well-defined transition-temperatures. These different forms are conveniently named, in the same way as the various forms of iron, by Greek letters, starting with the form which is stable at the lowest temperatures.

The crystalline forms of these modifications, and the published data in reference to the transition-temperatures, are set out in the following table.

TABLE I.

Changes of State in Ammonium Nitrate.

Form of salt.	Crystalline system.	Change of state.	Transition-temperature.
Liquid	—	ϵ to liq.	165—166°, 165°, 168°, 165·2°.
ϵ	Cubic	δ to ϵ	127°, 124—125°, 124°, 123·5—125·5°, 125·6°, 122·6°, 126·2°, 124·0—125·6°, 125·0°, 125·2°.
δ	*Rhombohedral	γ to δ	87°, 82·5—86°, 81°, 82·5—86·5°, 82·8°, 83·0°, 86·°, 85·5°, 84°, 84°, 82·26°.
γ	†Rhombic	β to γ	36°, 31—35°, 35°, 31—35°, 32·4°, 32·2°, 35·0°, 35·0°, 32·5°.
β	Rhombic		
α	Tetragonal	α to β	−16°, −18°.

* Or tetragonal. † Or monosymmetric.

In view of the fundamental character of these constants and of the fact that the temperatures are all easily accessible, a redetermination was made which has had the effect of fixing the freezing

point with an estimated error of a few tenths of a degree at 169·6°, whilst the three upper transition points have been determined probably within a few hundredths of a degree at 125·2°, 84·2°, and 32·1°.

I. *Freezing Point at* 169·6°.

The difficulty of determining the correct melting point or freezing point of the salt, and the fact that values much below the correct figure have so often been recorded, arise from two characteristic properties of the salt, namely, the very great sensitiveness of the freezing point to the influence of small quantities of moisture (details in reference to which will be given in a later paper) and the tendency of the salt to retain its moisture even when attempts are made to remove it by somewhat drastic methods.

On account of these properties of the salt, we obtained in our earlier experiments a long series of concordant values for the freezing point, which were afterwards proved to be more than 2° too low. These freezing points were determined by observing the arrest of temperature which occurred immediately after crystallisation had begun in about 40 grams of the molten salt, the salt being stirred vigorously in a glass tube surrounded by an air-jacket in a bath of boiling water in order to prevent over-rapid cooling. The temperatures were measured by a thermometer graduated in fifths of a degree from 0° to 200°, and recently re-standardised to 0·02° at the National Physical Laboratory; this thermometer was of the compensated type, and the zero had remained constant within 0·02° over a period of about ten years. Two auxiliary thermometers were used to record the temperatures of the "exposed column" of mercury inside and outside the glass tube containing the salt. A series of freezing points determined in this way gave very concordant figures, the corrected values being as follows:

166·95°, 166·95°, 166·90°, 167·15°, 167·0°. Mean, 167·0°.

This was the freezing point of a sample of the salt which had been recrystallised twice from water and dried, first in a steam-oven during several hours, and then during a day and a night over sulphuric acid in a desiccator exhausted with the help of a Gaede mercury pump.

Doubt was first thrown on the correctness of these readings when it was discovered that a commercial sample of ammonium nitrate which had been dried and ground, and then re-dried in the usual way in the laboratory, gave a freezing point of 168·8°, that is, nearly two degrees higher than our best laboratory specimen of the salt. As this higher freezing point could obviously not be due

to impurities, which would tend to lower the freezing point of the salt, it could only be attributed to the fact that the drying had been accompanied by a grinding which was absent in the laboratory process of purification already described.

In order to secure equally favourable conditions in the laboratory, the purified salt was heated in a steam-oven, cooled, and crushed in a mortar, and left overnight in a vacuum desiccator, this cycle of operations being repeated three or four times. A series of freezing points of material prepared in this way gave the following figures:

169·16°, 169·14°, 169·04°, 169·05°, 169·06°. Mean, 169·09°.

The first two values were for ammonium nitrate from Hopkin and Williams, twice recrystallised; the next two are for the same sample after storing for some weeks in a desiccator over calcium chloride; the last value is for a commercial sample of Norwegian nitrate recrystallised from water and dried by the method just described. These experiments showed that the freezing point of the salt was at least 169·1°, and might be as high as 169·2° in view of the first two values recorded in the list.

A further improvement in the freezing point was effected by sealing up in an exhausted flask, connected with a bulb of phosphoric oxide, some of the salt prepared as described above. The nitrate was shaken up repeatedly to expose a fresh surface, and at the end of a week the freezing point was determined. In plotting the cooling curves for these determinations of the freezing point, two modifications were made in the practice previously adopted, namely, (i) the outer water-jacket was kept at 80° instead of 100° in order to reduce the amount of water vapour round the apparatus; (ii) the stirring of the molten salt was stopped as soon as the temperature showed signs of becoming steady, in order to reduce the loss of heat from the molten mass, and so to prolong as much as possible the horizontal arrest in the cooling curve. The freezing points determined in this way were

169·58°, 169·55°.

After three months' further drying by phosphoric oxide, no further rise of the freezing point was produced, but, on the contrary, it appeared to have receded slightly. The freezing point of the pure dry salt may therefore be placed at **169·6°**. If the freezing point of the salt is expressed in whole numbers, the figure 170° is more exact than any hitherto given, since the experimental numbers recorded above are unlikely to be too high, but may still be slightly below the true maximum figure.

The drying of ammonium nitrate, which is not really a difficult

operation when dealing with the solid salt, cannot be effected merely by stronger heating, since the salt, which begins to decompose at 200°, retains even at this temperature the moisture produced by decomposition. Thus, two samples, which had been heated to vigorous effervescence at 225°, froze at 166·8° and 167·0° when cooled again to the freezing point of the molten salt. Again, a sample of the nitrate which melted originally at 169°, froze at 165·5° after being heated to 230° to 240° for a few minutes, and at 163·4° after a second heating. The molten salt, indeed, appears to cling to its water quite as tenaciously as concentrated sulphuric acid, and it is only by grinding the solid to a fine powder that complete drying is readily effected.

II. *Transition-temperature at* 125·2°.

When the molten salt is allowed to cool from the melting point in a tube provided with a thermometer dipping into the salt, the highest of the transition-temperatures referred to in table I gives rise only to a retardation of cooling at about 125°. In order to produce slower cooling and to secure, if possible, a horizontal arrest in the cooling curve, in spite of the poor thermal conductivity of the salt, the following method was adopted. About 90 grams of the purified salt were melted and poured into a small beaker, which was lowered into the centre of a vacuum-jacketed cylinder. A standard thermometer was inserted, and the salt was allowed to set round the bulb. The stem of the thermometer passed through a large rubber stopper, which served to close the top of the cylinder and so prevent loss of heat by convection to the outer air. The cylinder, in its turn, was immersed as far as possible in a bath of hot water, stirred mechanically, and maintained at a fairly constant temperature by a flame. A Bunsen valve was provided for the escape of air by expansion from the cylinder, whilst two auxiliary thermometers gave the temperatures of the "exposed column" of the standard thermometer. An attempt was made to retard the cooling still further by exhausting the air from the interior of the cylinder, but this procedure did not appear to serve any useful purpose, and was abandoned, because of the additional trouble caused by the frothing up of the salt to a porous mass during exhaustion. When observing the transition point at 125°, the temperature of the outer water-bath was maintained at 95°, but it was then generally allowed to cool to 75° in order to observe the further transition at 84°, to which reference is made in Section III below. The readings obtained in this way with air in the vacuum cylinder were 125·2°, 125·6°, 125·8°, 125·1°, 125·6°, 125·2°, whilst

with the air exhausted from the cylinder the readings were 125·2° and 125·4°. The mean of the whole series is 125·4°. Zawidzki (*Zeitsch. physikal. Chem.*, 1903, **47**, 721) obtained a mean value of 125·0° for arrests in the cooling of ammonium nitrate, alone and mixed with silver nitrate.

In the case of the transition point at 84°, the poor conductivity of the salt may be compensated by stirring the powder in a small revolving drum heated externally by means of a vapour-jacket, but this method cannot be employed at the higher temperatures, as the powder begins to cake into tough lumps. A much more effective method of securing good conduction during heating and cooling consists in stirring the powdered salt in a bath of liquid not differing too widely from it in density. The liquid selected for this purpose was a mixture of tribromoethane (D 2·62; b. p. 188°) and xylene (D 0·86; b. p. 140°), the density of ammonium nitrate at this temperature being about 1·6. Good results were also obtained by using nitrobenzene (D 1·22; b. p. 211°). This method of improving the thermal conductivity has the advantage that the thermometric measurements can be made within a maximum of accuracy. The procedure was as follows. The liquid was made into a "mush" with powdered ammonium nitrate in a glass tube 20 cm. long and 3·7 cm. in diameter, provided with a stirrer and a split cork to carry a standard thermometer; as before, two auxiliary thermometers were used to record the temperature of the "exposed column" of mercury. The glass tube was surrounded by a metal cylinder 20 cm. long and 5 cm. in diameter, closed at the top with cotton wool, and forming a narrow air-jacket round the tube. This cylinder was supported by a bung in the axis of a larger metal cylinder, 32 cm. long and 10 cm. in diameter, containing paraffin of high boiling point to serve as a heating or cooling bath, and provided also with a thermometer. In plotting a heating or cooling curve, the paraffin bath was adjusted by hand to a temperature a few degrees above or below the transition point. The "mush" in the inner tube was stirred at intervals of thirty seconds to two minutes, according to the velocity of heating or cooling, and the thermometer was read immediately after.

The arrest-temperatures observed in this way during heating and cooling, together with the conditions under which the heating and cooling were carried out, are shown in table II.

TABLE II.

Arrest-temperatures of Ammonium Nitrate suspended in a bath of Liquid.

	Arrest-points (corrected).	Temperature of outer bath.	Composition of liquid.
Heating:	125·21	130°	Nitrobenzene.
	125·16	140	Xylene and ethylene bromide.
	125·38	140	Xylene and ethylene bromide.
	125·22	130	Xylene and tribromoethane.
	125·25	130	Nitrobenzene.
Mean	125·24°		
Cooling:	125·27°	120°	Xylene and ethylene bromide.
	125·21	120	Xylene and ethylene bromide.
	125·09	120	Xylene and tribromoethane.
Mean	125·19°		

These values may be compared with those given by Vogt (*Physikal. Zeitsch.*, 1911, **12**, 1129), who obtained with a dilatometer the upper and lower limits 125·25° and 125·13°, mean 125·2°. The eight values now recorded range from 125·09° to 125·38°. The mean of the five readings obtained by heating the salt is 125·24°, whilst the mean of the three readings obtained by cooling is 125·19°. The general mean of all the readings is 125·22°, and this is probably the best value for the transition-temperature. In view, however, of the difficulty of reading the temperatures to 0·01°, we prefer to give the transition-temperature to a tenth of a degree at **125·2°**.

III. *Transition-temperature at* 84·2°.

The transition at 84° is accomplished by an abrupt expansion which frequently made itself manifest by fracturing the glass vessel in which a cast sample of nitrate was being cooled. There is, however, a very strong tendency for over-cooling to occur, and in many cases the salt was cooled to 32° without any indication that this change of crystalline form had taken place. In order to ensure the conversion of the δ- into the γ-form, it was necessary to inoculate the surface of the block with particles of the salt which had been heated to 60°, and to assist the conversion by scratching the surface with a sharply pointed glass rod. Even under these conditions, the over-cooling was usually very pronounced; the change of crystalline state (even in the vacuum-jacketed apparatus used successfully to record the change of state at 125°) only began when the temperature had fallen to 82° or below, and the latent heat was then not sufficient to restore the temperature to the transition point or to produce a horizontal arrest in the cooling curve. In

every case, therefore, the transition merely produced a sinuous curve, the highest temperature recorded for the maximum on this curve being 82·7°.

The first well-marked arrest of temperature at the transition point was observed when heating a sample of the powdered salt in a machine in which the nitrate was thrown over and over in such a way that the bulb of a thermometer was constantly bathed in the falling nitrate. A small machine in which this principle was embodied gave well-defined arrests on heating at 84·3°, 84·2°, 84·3°, and 83·3°, the first three values being concordant within one-tenth of a degree. It is remarkable that this transition-temperature, which was found to be so exceptionally difficult to locate by the methods first employed, proved to be by far the easiest of the transition points to determine exactly when once the proper conditions were established.

The most favourable conditions for determining this transition point were those already described in connexion with the change of state at 125·2°, namely, to compensate for the lack of thermal conductivity by stirring the powdered salt in a bath of liquid of almost equal density. The liquid used for this series of experiments was a mixture of ethylene bromide (D 2·18; b. p. 131°) and xylene (D 0·86; b. p. 140°). Special precautions were again needed to prevent "lag" in the change of state; the "mush" was therefore inoculated during heating with crystals heated to 100°, and during cooling with crystals heated to 60°. The inoculation was carried out just before reaching the transition point, and was followed by gentle stirring. The arrest points recorded in this way, which are lower than the mean of Zawidzki's arrests at 85·4°, but higher than the dilatometric readings 82·16° to 82·36° of Vogt, are set out in the following table:

TABLE III.

Arrest-temperatures of Ammonium Nitrate suspended in a Bath of Liquid.

Arrest-points (corrected).		Temperature of outer bath.	Composition of liquid.
Heating:	84·20°	90°	Xylene and ethylene bromide.
	84·16	90	" "
	84·25	90	" "
	84·20	90	" "
Mean	84·20°		
Cooling:	84·28°	Falling slowly.	Xylene and ethylene bromide.
	84·13	" "	" "
	84·18	" "	" "
Mean	84·20°		

In this case, the means of the four values obtained during heating and of the three values obtained during cooling are identical. The transition point may therefore be fixed, probably within a few hundredths of a degree, at 84·20°, or may be given to a tenth of a degree as **84·2°**.

IV. *Transition-temperature at* 32·1°.

(a) *Heating and Cooling Curves.*—The transition-temperature in the neighbourhood of 32° is more easily observed than either of those occurring at a higher temperature, since a prolonged arrest in the neighbourhood of 32° can always be detected when the nitrate is cooled through this temperature; indeed, both this arrest and that at 84° are constantly encountered when the nitrate is handled commercially. In spite of this fact, exceptional difficulty is experienced in securing an exact determination of this transition-temperature. This difficulty was ultimately traced to the fact that over a range of about a quarter of a degree on either side of the true transition point, the velocity of change of state is so slight as to be practically imperceptible, with the result that the conversion usually takes place at a temperature definitely below the transition point on cooling and at a temperature definitely above it on heating.

Large numbers of cooling curves were plotted in order to determine this transition-temperature accurately. In some experiments only a sinuous cooling curve was obtained, but in others well-marked horizontal arrests were recorded at the following temperatures:

Cast blocks	31·9°, 32·0°, 32·0°.
Pressed blocks	31·7°, 31·5°, 31·4°, 31·8°.
Loose crystals	31·6°.

Horizontal arrests were also recorded, sometimes at lower temperatures, for example, 31·0°, 29·5°, 29·6°.

Arrests during heating were always at a higher temperature, and the curves were generally of a sinuous form, rising to a maximum value before falling again to a minimum approximating to the transition-temperature of the salt. These minima in the heating curves were observed at the following temperatures:

Cast blocks	33·2°.
Pressed blocks	33·8°, 33·1°, 33·2°.

In one experiment in which the sample had become very much over-heated before the change of state set in, a still higher reading was obtained at 35·3° (compare Zawidzki, *loc. cit.*, who obtained

an average of 35·0° for seven arrests *in heating* ammonium nitrate alone and mixed with silver nitrate).

In view of the fact that the horizontal arrests or maxima in the cooling curves were always very much more fully developed than the minima in the heating curves, it was believed that the former could be assumed to give a correct value for the transition-temperature which was located provisionally at 32°; actually, however, the data now quoted can only be used to prove that the transition-temperature lies within certain limits, for example, between 32·0° and 33·1°, and it was not possible to secure an absolute determination by this method in view of the fact that in no case were the arrests on heating and cooling within one degree of each other.

Attempts to secure more accurate readings of these transition-temperatures by using larger quantities of nitrate up to a kilogram resulted in failure, the conductivity of the salt being so low as to prevent the effective flow of heat from one part of the mass to another; better results were, indeed, always obtained by heating or cooling much smaller quantities of ammonium nitrate, insulated as carefully as possible, for example, in a vacuum vessel, in order to reduce the rate of heating or cooling to a minimum. A distinct improvement in the heating curves was, however, obtained, as in the case of the transition at 84°, by stirring about 700 grams of powdered nitrate in a small drum, surrounded by a steam-jacket, in such a way as to produce a constant flow of nitrate past the thermometer. By using this method, the following arrests in the heating curves were recorded:

32·6°, 32·75°, 32·7°, 32·9°, 33·0°.

These readings are definitely lower than those recorded previously when cast or pressed blocks of the nitrate were heated, but no improvement could be effected in the cooling curves, so that there still remained a gap of about 0·6° between the highest arrest on cooling and the lowest arrest on heating.

The method of stirring the powdered nitrate in a bath of liquid of equal density, which had proved so successful at the higher temperatures, was a complete failure when applied to the determination of the transition-temperature at 32°. The temperature recorded on the thermometer immersed in the liquid frequently failed to show any arrest at all. Even after inoculation, the cooling curves were extremely erratic, and only on two occasions were satisfactory arrests observed at 31·8° and at 31·6°; on no occasion was an arrest observed in the heating curve. It may be noted, however, that Müller (*Zeitsch. physikal. Chem.*, 1899, **31**, 354) obtained a satisfactory arrest at 32·2° by cooling from 80° a mix-

ture of 100 grams of ammonium nitrate with 15 to 20 grams of water, and that this temperature lies within 0·1° of our final value for this transition point.

(b) *Experiments with the Dilatometer.*—The unexpected difficulties which were encountered in trying to determine the exact position of the transition-temperature at 32·1° can be traced to the relative slowness with which the change of state takes place immediately above or below the transition point, even when assisted by inoculation, as contrasted with the much greater velocity of the changes at 84° and 125°.

This is in accordance with the general rule that changes of this character become more and more sluggish as the temperature falls, by reason of the decreasing mobility of the molecules and the increasing resistance which the rigidity of the material opposes to molecular rearrangement. Under such conditions, the thermal method becomes difficult or impossible, and it is usually necessary to fall back on some method of determining the transition-temperature in which ample time can be allowed for the change of state to reveal itself. In the case of ammonium nitrate, the most promising method was to follow, by means of a dilatometer,* the expansion or contraction which accompanies the change of state, instead of relying on the absorption or liberation of latent heat to produce an arrest in the heating or cooling of the salt.

Experiments which were made on these lines gave us our first trustworthy value for this transition-temperature, and also provided valuable information as to the velocity of the change in the immediate neighbourhood of this point.

The solid used in the dilatometer was made by fusing pure, dry ammonium nitrate, pouring into a mortar, breaking the cast lump into pieces about 0·3 cm. in diameter, and sieving to free it from dust. This form of the salt was used in order to secure good thermal contact between the solid and liquid, and, at the same time, to avoid the risk of fracturing the bulb by the sudden expansion of a closely-packed powder. The dilatometer held about 60 c.c., and the bulb was sealed off after filling about three-quarters full with fragments of nitrate. The liquid was a paraffin of high boiling point which had been treated with concentrated sulphuric acid to free it from olefines, and then dried over metallic sodium; it was introduced in an air-free condition by making use of the apparatus shown in Fig. 1 of a paper by Wade and Merriman (T., 1912, **101**, 2430).

In a dilatometer filled in this way, there are at the transition-

* Compare van't Hoff, *Zeitsch. physikal. Chem.*, 1895, **17**, 130, and "Vorlesungen," 1898, vol. i., p. 18.

temperature two alternative positions for the meniscus; one, which may be called $V\beta$, is the position when all the nitrate is still in the stable low temperature or β-form; the second, which may be called $V\gamma$, is the position to which the meniscus rises when all the nitrate has been converted (without change of temperature) into the lighter γ-form. The position $V\beta$ can be determined by heating the dilatometer from the atmospheric temperature to a point just below the transition point; $V\gamma$ can be determined by heating the dilatometer, say to 50°, until the whole of the nitrate has passed into the γ-form, and then cooling it to a point immediately above the transition point at 32°; very little extrapolation is then required to give the exact position of these two points.

In using this method to determine the transition-temperature of ammonium nitrate, it is essential that the dilatometer should contain both forms of the salt, in order that change of state may take place quite readily in either direction. This condition was secured by heating the dilatometer to 50°, when the meniscus rose to a point well above $V\gamma$; on immersing the dilatometer in cold water, part of the salt reverted from the γ- to the β-form, a change which was revealed at once by the appearance of white patches on the lumps of nitrate; this change took place long before the contents of the bulb as a whole had time to cool to the transition-temperature. Having made sure in this way that the nitrate in the bulb contained a substantial proportion both of the β- and of the γ-forms of the salt, it was possible to find a range of temperatures (just above the transition point) at which the meniscus tended to settle down in the neighbourhood of $V\gamma$ by reason of the complete conversion of the contents to the γ-form, and a range of temperatures (just below the transition point) at which the meniscus would settle down in the neighbourhood of $V\beta$, owing to the complete conversion of the nitrate to the β-form.

The actual behaviour of the dilatometer when heated at different temperatures after the preliminary treatment described in the preceding paragraph was as follows:

(i) When the dilatometer was immersed in a thermostat at 32·2°, the meniscus settled down very quickly to a definite position between $V\beta$ and $V\gamma$, and during the course of two hours showed no tendency to rise to $V\gamma$ or to fall towards $V\beta$. The change of state appeared, in fact, to be arrested at the point to which it had been brought by the more drastic preliminary treatment of the salt. A precisely similar behaviour was observed at 32·1°, 32·0°, 31·9°, 31·8°, and 31·7°.

(ii) When the temperature of the thermostat was reduced to 31·6°, the meniscus for the first time began to show a tendency to

fall towards $V\beta$, although the change at this temperature was so slow as to be almost imperceptible; on repeating the experiment with the thermostat set to 31·5°, however, a definite movement towards $V\beta$ could be seen. These two temperatures are therefore definitely below the transition point of the nitrate.

(iii) When, on the other hand, the temperature of the thermostat was raised to 32·3°, a definite but exceedingly slow upward movement of the meniscus towards $V\gamma$ was observed, and a more pronounced movement when the temperature was raised to 32·7°.

These experiments, on account of the extreme sluggishness of the change of state in the immediate neighbourhood of the transition point, failed to fix the exact position of this temperature, although they served to locate it between 31·6° and 32·3°. These two limits agree quite closely with those arrived at from a study of the cooling and heating curves, which had shown arrests below and above two corresponding limits at 32·0° and 32·6°; rather closer limits were recorded by Vogt, who observed equal and opposite slow changes of volume at 32·40° and 32·62°.

(c) *Quantitative Experiments with the Dilatometer.*—In order to determine the exact position of the transition point, a series of quantitative experiments was made on the velocity of the change of state as shown by observations with the dilatometer at temperatures above and below the transition-temperature.

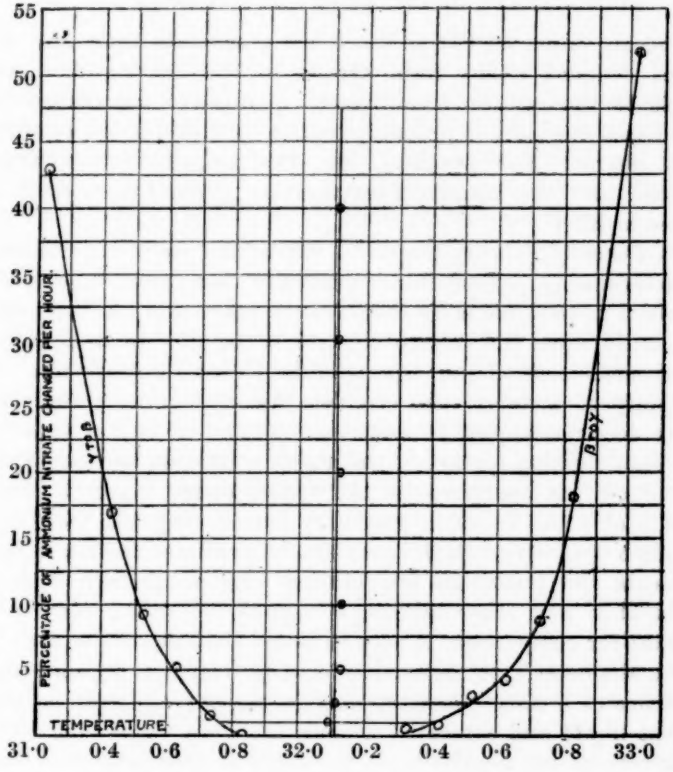
The preliminary treatment of the nitrate was much the same as in the previous experiments, and was carried out as follows. The two extreme positions of the meniscus at the transition-temperature were first located on the scale of the dilatometer, as follows:

$$V\beta = 20 \text{ cm.}; \quad V\gamma = 48 \text{ cm.}$$

Starting with cold nitrate in the β-form, the dilatometer was next immersed in a bath of water at 34° in order to initiate the change from the β- to the γ-form. At this temperature (on account of thermal expansion), the two extreme positions of the meniscus would be about 22 and 50 cm.; when, therefore, the meniscus had risen to about 36 cm. on the scale of the dilatometer, it was clear that the two forms were present in roughly equal quantities, whilst the thermal conditions of the dilatometer and its contents had not been seriously disturbed.

After this preliminary treatment, the dilatometer was immersed in a thermostat set to a definite temperature just above or below the transition point. Thermal equilibrium was quickly established, and exact measurements could be made of the rate of movement of the meniscus consequent on the change of state from

β to γ, or vice versa; the uniformity of this movement, over considerable periods of time, was such as to justify the view that the rates recorded in heavy type in table IV are definite physical constants of the change of state over the range of temperatures from 31·2° to 33·0°. The readings represent the movement in mm. of the meniscus during successive intervals of ten minutes. The mean steady velocities (obtained by averaging the numbers which are shown in heavy type in table IV) are recorded in similar units.



The final column shows the percentage of the salt which would undergo change of state in one hour, as deduced from the volume changes recorded in the previous columns. The thermometer readings are given to tenths of a degree, but are all subject to a correction of +0·03°. It is remarkable that at temperatures a whole degree above or below the transition point, nearly an hour is required to change half of the material from the β- to the γ-form, or vice versa.

When all these velocities are plotted out in a diagram, as in

the figure, a curve is obtained which is almost symmetrical on either side. According to the well-known principle which is used in determining the "critical volume" of liquids and vapours, the transition-temperature may be determined accurately by ruling a series of horizontal lines across the velocity diagram, reading off the temperatures given by the intercepts of these lines with the curve, and working out an average value for each pair of temperatures. These averages, as set out in table V below, are as follows:

32·09°, 32·11°, 32·13°, 32·13°, 32·12°, 32·11°, 32·11°.

The mean value, 32·11°, is much more accurate than any of the values deduced either from arrests in the heating and cooling curves of the salt or from merely qualitative observations with the dilatometer, and is probably correct to within a few hundredths of a degree. For practical use, the second decimal may be omitted, and the transition-temperature given to one-tenth of a degree as **32·1°**.

(d) *Form of Velocity Curve.**—Whilst the use of the dilatometer in determining transition-temperatures has been a well-known standard method for more than twenty years, and has been applied repeatedly when the change of state is too slow to be followed by the thermal method (see especially E. Cohen's experiments on the allotropy of metals); the complete velocity curve shown in the figure does not appear to have been plotted in any of these cases. The most striking feature of this curve is its complete symmetry, as proved by the constancy of the temperatures shown in the last column of table V, which only vary over a range of ±0·02°. This complete symmetry, which could not be predicted, makes it possible to locate the transition temperature very accurately, and it is doubtful if any other method is capable of giving equally exact results; for comparison, it may be noted that the use of the "rectilinear diameter" to determine critical volumes depends on the existence of a skew-symmetry only in the curve of specific volumes for the liquid and saturated vapour.

In view of the regularity of the curve it is of interest to inquire into its mathematical form. The data now recorded can be expressed by the equation

$$\pm(t-t_0)=\log_{10}(\sqrt{v}+1),$$

where t = temperature,

t_0 = transition temperature,

v = velocity of change (percentage changed per hour).

* Added 6/12/19.

The agreement of this formula with the experimental results is shown in the following table:

v.	$\pm(t-t_0)$ obs.	$\pm(t-t_0)$. calc.
1	0·33°	0·30°
2·5	0·41	0·41
5	0·50	0·51
10	0·62	0·62
20	0·72	0·74
30	0·79	0·81
40	0·86	0·86

(e) *Anomalies in the Heating and Cooling Curves.*—At a very early period in the investigation, it was noticed with some surprise that very steady arrests of heating and cooling might occur at temperatures which were obviously not exact transition points, since they were scattered over a considerable range on either side of a mean value, which could be regarded provisionally as the correct transition-temperature. This was an anomaly for which no explanation could be suggested at the time.

General experience in such matters has shown that when dealing with rapid transitions, such as are observed in iron at 895° and 766°, the arrest in the cooling curve becomes blurred whenever liberation of latent heat fails to compensate for loss of heat by cooling; a lowered arrest point is therefore nearly always revealed by its sinuous character. In dealing with ammonium nitrate, many sinuous arrests have been observed at temperatures either below or above the real transition point, but in several cases the arrests recorded at these lower or higher temperatures were perfectly sharp.

These observations can all be interpreted in the light of the data now given for the velocity of change of state. Thus, in the first place, it is obvious that since this velocity of change is imperceptible from 31·8° to 32·3°, there can be no marked liberation or absorption of latent heat and no arrest in the cooling or heating between these limits. Outside these limits of temperature, the flow of latent heat may arrest the cooling or heating, but the conditions are such that the arrest point cannot be regarded as a fixed temperature, but must be considered as a variable temperature depending directly on the rate of heating or cooling. Thus, taking the latent heat of the transition as 5·02 calories per gram, and the velocities of change of state as recorded in table IV, the temperatures of arrest for the different rates of cooling and heating shown in column 2 of table V are given in columns 3 and 4 of that table.

Table IV.

Velocity of Change of State, above and below 32·1°.

Temperature.*	Motion of meniscus, in mm. per 10 minutes.													Mean rate in mm. per 10 minutes.	Percentage changed per hour.
31·2°	33·8	25·0	20·0	21·0	—	—	—	—	—	—	—	—	—	20·0	42·8
31·4	8·4	9·0	8·3	8·2	8·1	7·5	7·5	—	—	—	—	—	—	7·9	16·9
31·5	11·0	2·1	2·2	3·0	3·7	4·2	4·5	4·5	4·3	4·7	4·3	4·0	—	4·3	9·2
31·6	1·4	1·2	1·9	1·9	2·0	2·2	2·5	2·4	2·4	2·4	2·3	—	—	2·4	5·2
31·7	0·8	0·8	0·4	0·4	0·7	0·7	0·6	0·7	0·6	0·6	0·6	0·6	—	0·64	1·4
31·8	10·5	1·1	0·3	0·1	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
32·0	—	0·1	0·1	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
32·2	6·5	0·5	0·0	0·0	0·0	0·0	0·0	0·1	0·0	0·0	0·0	0·0	0·0	0·0	0·0
32·3	7·0	1·2	0·3	0·7	0·3	0·2	0·3	0·2	0·2	0·2	0·2	0·3	0·2	0·23	0·5
32·4	—	1·7	1·6	0·1	0·4	0·2	0·2	0·3	—	—	—	—	—	0·30	0·7
32·5	13·7	4·7	3·0	2·3	2·2	1·7	1·5	1·5	1·4	1·4	1·2	1·2	—	1·4	3·0
32·6	4·8	7·6	3·5	2·3	2·8	2·5	2·0	1·7	1·9	1·7	1·6	—	—	1·9	4·1
32·7	9·0	7·9	7·0	5·7	5·0	4·8	4·0	4·0	4·0	4·0	—	—	—	4·0	8·6
32·8	†8·4	†8·0	†7·7	†7·2	†7·2	†7·2	†6·8	†6·8	†6·4	†6·3	†6·6	†6·6	†6·6	8·4	18·0
33·0	21·7	22·9	23·8	24·3	24·4	24·1	—	—	—	—	—	—	—	24·1	51·7

* Correction at each temperature = + 0·03°.

† 8 minute intervals.

TABLE V.

Velocity of Change of State of Ammonium Nitrate at Different Temperatures.

Per cent. changed per hour.	Rate of cooling or heating. Calories per gram per hour.	Temperature (arrest-points). Cooling.	Heating.	Average temperature.
1	0·050	31·75°	32·42°	32·09°
2·5	0·126	31·69	32·52	32·11
5	0·251	31·63	32·63	32·13
10	0·502	31·51	32·75	32·13
20	1·00	31·40	32·84	32·12
30	1·51	31·32	32·90	32·11
40	2·01	31·25	32·96	32·11
			Mean	32·11°

The arrest points shown in the table are the temperatures at which the latent heat, liberated by a change of state proceeding with known velocity, would exactly balance the heat gained or lost by radiation, conduction, etc. Imperfect conduction of heat in the mass may displace these temperatures still further from the true transition point, and at the same time destroy the sharpness of the arrests. The latter phenomenon is observed also in the transitions at 84° and at 125°, where sinuous arrests at abnormally low temperatures are frequently observed, but the velocity of change of state at these two points is so much greater that a prolonged or "horizontal" arrest has never been observed, except at a temperature agreeing very closely with one or other of these transition points.

Summary.

(1) The freezing point of ammonium nitrate is very sensitive to the influence of traces of moisture; by careful purification and drying it has been raised to **169·6°**.

(2) The highest of the transition points has been determined from the arrests of temperature on heating and cooling the salt when suspended in a liquid of similar density. The temperatures recorded were: on heating, 125·24°; on cooling, 125·19°; mean value, **125·2°**.

(3) The second transition point was determined by the same method, the observed temperatures being: on heating, 84·20°; on cooling, 84·20°; mean value, **84·2°**.

(4) The lower transition point cannot be determined in this way, as the change of state is too slow to be detected over the range from 31·8° to 32·2°. It was determined dilatometrically by measuring the rate of change over a range of temperatures; the

curve of velocities proved to be symmetrical, and the transition-temperature was therefore found by taking the average of pairs of temperatures at which the change proceeded with equal velocities in opposite directions. In this way, the transition-temperature was fixed at **32·1°**.

(5) The form of the velocity curve for the change of state can be expressed by the simple empirical equation

$$\pm(t-t_0)=k\log_{10}(\sqrt{v}+1).$$

(6) The arrest points due to the change of state at 32·1° never coincide with this temperature, the arrest point being determined by the rate of loss or gain of heat. A table is given showing the temperatures of arrest on cooling or heating at fixed rates expressed in calories per gram per hour.

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CXXXII.—*The Production of Methyl Ethyl Ketone from* n-*Butyl Alcohol.*

By ALBERT THEODORE KING.

IN this conversion, the usual series of steps has been employed of dehydration, re-hydration of the resulting alkylene to the secondary alcohol, and, finally, dehydrogenation of the latter to give the corresponding ketone:

$$R\cdot CH_2\cdot CH_2\cdot OH \longrightarrow R\cdot CH_2{:}CH_2 \longrightarrow R\cdot CH(OH)\cdot CH_3 \longrightarrow R\cdot CO\cdot CH_3.$$

No details appear to have been published hitherto regarding the hydration of butylene to the secondary alcohol, and although the first and last of the above stages have in this particular case been elsewhere described, the comparative results now obtained seem worthy of being placed on record also.

Dehydration of n-*Butyl Alcohol.*—Each of the three possible butylenes,

$$\underset{\alpha\text{-}}{CH_3\cdot CH_2\cdot CH{:}CH_2} \qquad \underset{\beta\text{-}}{CH_3\cdot CH{:}CH\cdot CH_3} \qquad \underset{\gamma\text{-}}{(CH_3)_2C{:}CH_2},$$

has been identified by previous observers in the product of dehydration, the composition of which would appear to depend both on the nature of the dehydrator and on the temperature employed. Thus Ipatiev (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 577), with

alumina as catalyst, at 500° obtained a gas containing 25—30 per cent. of α-butylene, the rest being γ-butylene; the latter was attributed to the presence of *iso*butyl alcohol in the material employed. Senderens (*Ann. Chim. Phys.*, 1912, [viii], **25**, 449), using aluminium sulphate at 300°, obtained α-butylene with 27 per cent. of γ-butylene. Le Bel and Green obtained on dehydration with zinc chloride a product free from γ-butylene and containing 80 per cent. of β-butylene and 10 per cent. of α-butylene (*Bull. Soc. chim.*, 1881, [ii], **35**, 438).

In the present investigation, in which phosphoric acid on pumice was used, only slight differences were observed in the composition of the product at temperatures ranging from 280° to 400°. No γ-butylene was detected, and even at 280° the amount of α-butylene present, so far as was indicated by fractionation of the bromide, could only be slight. This method of dehydration, therefore, yielding reasonably pure β-butylene, gives a much more homogeneous product than those previously described.

Hydration of Butylenes.—The hydration of the three butylenes with sulphuric acid should theoretically proceed as formulated below:

$$\left.\begin{array}{l} CH_3\cdot CH_2\cdot CH{:}CH_2 \\ CH_3\cdot CH{:}CH\cdot CH_3 \end{array}\right\rangle \longrightarrow CH_3\cdot CH_2\cdot CH(OH)\cdot CH_3$$

$$(CH_3)_2C{:}CH_2 \longrightarrow (CH_3)_3C\cdot OH$$

This conversion in the case of γ-butylene has been described by Butlerov (*Annalen*, 1875, **180**, 245), who also records the very slow hydration of β-butylene, but without details of the isolation of *sec.*-butyl alcohol. Nor is the formation of the latter from α-butylene recorded; and this point is under examination, the present investigation dealing only with the behaviour of β-butylene.

The rapid absorption of β-butylene (as also of α- and γ-butylene) by concentrated sulphuric acid is well known, but by this action polymerisation, and not hydration, results. With diluted acid, the very slow action on keeping has been confirmed, but liquefied β-butylene, under its own pressure, agitated in contact with the acid, has been found to undergo absorption with ease. Polymerisation, which is marked at the higher concentrations, is very slight with 78 per cent. acid, and below this strength the reaction proceeds normally.

In one case, an absorption was observed of nearly 20 per cent. in excess of the butylene theoretically required to convert the acid to butylsulphuric acid, suggesting that the latter is capable of

catalysing the direct hydration of β-butylene. It is hoped to investigate this point further.

The diluted solution, on distillation, readily gives the secondary alcohol in good yield.

Dehydrogenation of sec.-*Butyl Alcohol.*—Reduced copper is recorded by Sabatier and Senderens as being particularly efficient in catalysing the dehydrogenation of secondary alcohols, these showing a conversion without complications, but incomplete owing to the reverse action also taking place in the presence of copper. They observed the formation from *sec.*-butyl alcohol of methyl ethyl ketone and pure hydrogen, without any accessory reaction, within the temperature range of 160—300° (*Ann. Chim. Phys.*, 1905, [viii], **4**, 433, 465). In the present work, the reverse action above referred to was perceptible, but only slight.

Experimental.

Preparation of β-Butylene.

The *n*-butyl alcohol distilled at 116—118°. It was gently boiled in a silica distilling flask attached to a 2·2 cm. copper tube 150 cm. in length, capable of giving, by electrical heating, temperatures, registered at the middle part, from 280° to 400°. This was packed with fragments of ignited pumice impregnated with glacial phosphoric acid. (This catalyst can be used indefinitely, its activity being renewed occasionally by burning a piece of phosphorus at the mouth of the tube, with a current of air passing through.) The unchanged alcohol and water formed were collected in a receiver with water-cooled reflux and with a syphon tube for the discharge of the condensate from time to time. The gaseous product, after scrubbing with 60 per cent. sulphuric acid to retain any γ-butylene, was absorbed in cooled bromine until the latter was nearly colourless. The product was then shaken with dilute alkali, dried with calcium chloride, and systematically fractionated. The following are typical results:

	(1).	(2).	(3).
Temperature	300—320°.	280—300°.	400°.
Dried product	75 grams.	114 grams.	120 grams.
Final fractions :—			
below 155°	(153—157°. 7 grams)	3·5 „	2 „
155—157°	—	9·0 „	8 „
157—159	60 „	92 „	98 „
159—161	3 „	3 „	5 „
residue	3 „	3·5 „	4 „

The boiling points of the three dibromides are: α-, 166°; β-, *cis*-form, 158°; *trans*-, 161°; γ-, 149·6°. Thus α-butylene is not present, even at the lowest temperature employed, in notable quantity. The low fraction, possibly indicating the presence of γ-butylene, was not appreciably increased in (2), in which washing with 60 per cent. acid was omitted, and these lower fractions were not in sufficient quantity to detect by further fractionation the presence of γ-butylene dibromide. Moreover, no *tert.*-butyl alcohol was obtained from the 60 per cent. acid used to wash more than 100 grams of gas. On dilution and distillation, it yielded only 3 grams of product, which proved to be mainly *n*-butyl alcohol carried over.

Much of the butylene formed dissolves in the butyl alcohol which escapes dehydration and condenses in the receiver. From this solution, more than 150 times its volume of butylene is expelled on raising to boiling point.

No side-reaction was observed in the dehydration. The unchanged alcohol layer, dried and fractionated, yielded, finally, 1—2 per cent. distilling below 116°, the rest passing over at 116—118°, and for continuous working the condensate was shaken with salt and the upper layer separated and used again, thus conserving the dissolved butylene.

Action of Sulphuric Acid on β-Butylene.

On bubbling the gas through concentrated sulphuric acid, rapid absorption took place, the liquid becoming warm and darkening in colour. A pale yellow upper layer formed, and when this had increased to about 10 c.c. in volume, it was separated, washed, and dried with calcium chloride. It had a slight odour of hydrocarbon, and, on distilling, boiled without any constancy from 140° to 300°. The sulphuric acid layer gave, on pouring into excess of water, a turbid liquid, from which a small quantity of oil separated, which gradually darkened and became very viscous. These products, presumably formed by polymerisation of the β-butylene, were not further investigated. No secondary alcohol was detected in the aqueous portion.

With diluted acid, even up to 78 per cent., no appreciable absorption took place when the gas was merely bubbled through. For absorption under pressure, the following procedure was used.

The gas was liquefied by passing through a worm cooled in a mixture of ice and salt, the outlet tube dipping under the acid contained in a stout-walled bottle, also cooled in ice and salt. This gave good condensation, bubbles of gas escaping only at rare

intervals. The bottle was then closed by a rubber stopper, wired down, and, after weighing to ascertain approximately the amount of butylene condensed, shaken in a mechanical shaker until the butylene layer had disappeared. In each case, 50 c.c. of pure acid were used with varying dilution, and the time occupied for absorption was roughly noted, with the following results:

Concentration. Per cent.	Butylene. Grams.	Time taken.
100	17	—
84·0	21	5 minutes
78·0	23	20 ,,
76·0	22	40 ,,
75·3	22	1 hour
72·5	19	1·6 hours
70·0	24	5 ,,
64·8	10	8 ,,
50·0	22	Little effect after 15 hours.

With pure acid, the absorption was complete in a few seconds. On pouring into ice, an oil separated which, after drying with calcium chloride, weighed 15 grams. It distilled from 140° to above 300° without boiling constantly at any point, like the product previously described. No secondary alcohol was present in the aqueous portion.

With 84 per cent. acid, the alcohol was the main product, but considerable polymerisation occurred. Moreover, the acid crystallised in the freezing mixture, causing inconvenience through blocking of the delivery tube. The freezing-point curve shows the range of concentration, having sufficiently low freezing point and also giving normal reaction in reasonable time, to be from 74·5 (f. p. −20°) to 78 per cent. (f. p. −20°). The concentration ultimately adopted was 75 per cent. With 78 per cent. acid, a trace of oil with a terpene-like odour was observable on dilution, this becoming imperceptible with the lower concentrations.

The rise of temperature was very marked with the higher concentrations. The pressures generated by the liquid butylene were approximately determined by a pressure gauge as follows:

12°	0·6 atm.
20	0·95 ,,
30	1·4 ,,
40	1·9 ,,

With 75 per cent. acid, the temperature did not reach 40°, and the operation is thus without risk.

To ascertain the extent of absorption, 76 per cent. acid, containing 92 grams of pure acid, was shaken with 63 grams of butylene (theoretical quantity = 51·5) for fifteen hours. The excess of gas was allowed to escape, and any in physical solution removed by

exhaustion, when 61 grams were found to have been chemically absorbed. About 90 per cent. of the theoretical quantity was, however, usually employed.

Hydrolysis of Butylsulphuric Acid.

Comparative experiments were made, using three portions of 50 grams from the same batch of butylsulphuric acid. These were respectively neutralised with sodium carbonate and treated with quantities of 50 and 25 grams of water. The liquids were distilled, and the distillates caught in graduated tubes and thoroughly shaken with salt solution and a slight excess of salt. The volumes of upper layer were 23 c.c., 23 c.c., and 22·5 c.c. respectively. With neutralisation as employed by Butlerov (*loc. cit.*), the alcohol distilled over very slowly with a large quantity of water. Distillation with the lesser quantity of water gave a distillate with only a small aqueous layer, the bulk being retained by the acid, but with a slightly lower yield, although no ether was detected in the product. Dilution with an equal weight of water was therefore adopted.

With this procedure, 51 grams of butylene yielded a distillate which, after salting out and drying with potassium carbonate, weighed 60 grams, that is, 89 per cent. of the theoretical on the crude material. From 150 grams of dried, undistilled product, after careful fractionation, were obtained as final fractions:

below 97·5°	3	grams
97·5—99·5°	131	,,
99·5—100°	8	,,
residue	5	,,

The fraction 97·5—99·5° was employed for conversion to ketone.

Dehydrogenation of sec.*-Butyl Alcohol.*

The procedure followed was substantially that of Sabatier and Senderens (*loc. cit.*). A copper tube 172 cm. long and 1·2 cm. in diameter was packed with copper oxide from wire kept in place with plugs of rolled copper gauze, and enclosed in a 2·5 cm. copper tube 135 cm. long wired for electrical heating. After reduction of the wire with ethyl alcohol vapour, and expulsion of the latter, *sec.*-butyl alcohol was distilled through from a silica flask at such a rate that the distillate passed through at the rate of about one drop a second. This was caught in a receiver cooled in ice-water. The hydrogen was evolved just too fast to allow the bubbles through a wash-bottle to be counted. The temperature remained

fairly constant throughout, the fluctuation on either side of 290° being never more than 5°.

In the first preparation, from 100 grams of alcohol, 104 of distillate were obtained. This contained water, formed from some unreduced copper oxide, and, on fractionating, 94 grams distilled at 73—75°, the mixture separating a small, lower layer of water. After drying with potassium carbonate, the bulk distilled at 79—81°.

Two hundred and fifty grams of alcohol gave an almost theoretical yield of dried, undistilled product, which gave the following fractions:

76—79°	5 grams
79—81	199 ,,
81—82	9 ,,
82—86	6 ,,
residue	12 ,,

Thus the conversion is upwards of 90 per cent.

The fraction boiling at 79—81° decolorised permanganate, but after stirring with about half a gram of powdered potassium permanganate for a short time, the colour persisted. On distilling off and drying thoroughly with potassium carbonate (the boiling point is very easily affected by traces of water), the ketone distilled almost completely within the range 80—80·6°.

The yield on the small scale from the crude butylene is about 70 per cent. of the theoretical, and with continuous working and recoveries this figure at least should be reached in the complete synthesis from *n*-butyl alcohol.

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CXXXIII.—*Conversion of the Simple Sugars into their Enolic and Ethylene Oxide Forms.*

By EDWARD FRANKLAND ARMSTRONG and THOMAS PERCY HILDITCH.

No group of compounds is more remarkable than that of the hexoses, on account of their extreme mutability. Glucose, for example, may be obtained in an α- and a β-crystalline form, and if either of these is dissolved in highly purified water the solution is all but stable. Yet if a trace of alkali is added, an equilibrated

mixture of the two isodynamic forms is practically instantaneously produced. The change has been specially studied by Lowry (T., 1903, **83**, 1314; 1904, **85**, 1551), and its character has been discussed also by one of the authors (T., 1903, **83**, 1305).

The more gradual change, also under the influence of alkali, from one hexose into another, within sections including as many as four members of the group (for example, glucose $\rightleftharpoons$ mannose $\rightleftharpoons$ fructose $\rightleftharpoons$ glutose), was brought to light through the painstaking labours of the late Lobry de Bruyn (*Rec. trav. chim.*, 1895, **14**, 156, 204). In this case, the transition has been assumed to involve the formation of an enolic form as an intermediate term. In the case of the hexoses the aldehydic form (aldehydrol) is commonly supposed to have but an ephemeral existence, and it is held that α- and β-glucose are butylene oxide or pentaphane derivatives corresponding with the two methyl glucosides. The latter, it is well known, are simultaneously produced by the action of a strong acid on glucose dissolved in methyl alcohol; a residue, long unexplained, has recently been shown to contain a third isomeric methyl glucoside, regarded by Fischer and by Irvine as the derivatives of an ethylene oxide form of the hexose.

Irvine and his school (T., 1915, **107**, 524; 1916, **109**, 1305, etc.) have shown that the new methyl glucoside is characterised by its capacity to condense with acetone, to reduce potassium permanganate solutions, and to undergo auto-condensation, and that the activity of the parent glucose from which it is derived far exceeds that of α- or β-glucose.

The observations we have to place on record relate to the changes effected in the simple sugars by acids and by alkalis, as measured both by means of the polarimeter and by means of increased liability to oxidation.

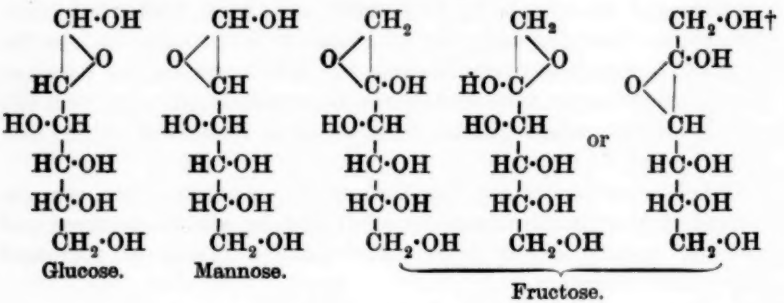
A solution of either α- or β-glucose in water (both well purified) is practically unaffected by permanganate. In acid solution, reduction of the permanganate sets in at once and at a definite rate under definite conditions; thus, under the standard conditions detailed in the experimental part, 10 c.c. of 1 per cent. of α- or β-glucose in $N/10$-hydrochloric acid solution decolorise 2 c.c. of $N/100$-permanganate solution at 25° in twenty-eight to thirty minutes. That the change is instantaneous is proved by the fact that the reducing power acquired is independent of the time during which the acid has acted, solutions containing acid which have been kept various times all having the same reducing power. The strength of the acid, however, is a factor in the change, the effect being less the weaker the acid and likewise the less concentrated the acid.

We consider that the active agent is the ethylene oxide modification of glucose,

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot CH\cdot OH^*$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \diagdown\diagup$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

The amount of the ethylene oxide form present is regulated by an equilibrium depending on the strength of the acid, but that it is small is shown by the fact that the optical rotatory power of glucose in an acid is the same as in an aqueous solution. The ethylene oxide form is reproduced as oxidation by the permanganate proceeds, as shown by the fact that fresh additions of permanganate solution are decolorised.

Mannose and fructose are affected by acids in a similar way, but the altered mannose solution acts far more rapidly than that of glucose; fructose is only slightly less active than mannose. For example, under precisely comparable conditions, whereas the reduction of permanganate by glucose occurs in twenty-eight to thirty minutes, that by mannose takes only from twelve to thirteen, and that by fructose sixteen to seventeen minutes.



In view of the close relation of the ethylene oxide forms of these sugars, it seems not improbable that one of the isodynamic forms is the more oxidisable, and that this is the form present in mannose.

The reduction of permanganate (as well as of methylene-blue and of indigo-blue) is also promoted by the addition of alkali. In

* At first sight the alterations involved in the conversion of butylene oxide into ethylene oxide or enolic forms of glucose appear somewhat far reaching when viewed only in the light of the conventional structural formulæ. If, however, structural models are prepared of the sugars on the lines of the Pope-Barlow hypothesis of close packing a more rational interpretation of the changes is realised.

† This form of fructose is present in sucrose according to Haworth and Law (T., 1916, 109, 1314).

this case, however, the change of the hexose is more gradual, as, within limits, the solution is the more active the longer the alkali has acted. The interactions in the three cases take place at corresponding rates, showing that in each case the same change is being studied. Under the experimental conditions observed, the reduction phenomena correspond only with the changes in structure which take place in the course of the first few hours, and it is unlikely that any far-reaching disturbance has occurred in the carbon chain beyond the atoms 1 and 2.

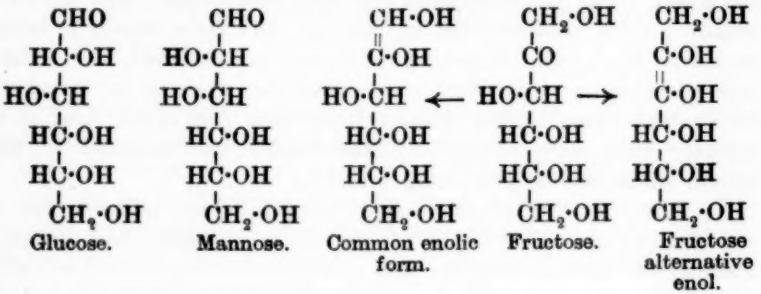
As shown by the polarimeter, the equilibrium between the α- and β-butylene oxide forms of the sugar is established instantaneously in alkaline solution, and subsequently the optical activity falls slowly, but it is still of considerable magnitude at the end of six hours. After this, it continues to fall, some fifteen to twenty days being required before the solution loses its activity. To judge from the slowness with which alkali acts as compared with acid, taking into account the instantaneous equilibrium of the α- and β-forms in the presence of alkali, it is clear that the latter are not concerned in the change. It therefore seems probable, so far as the effect produced by acids is concerned, especially in view of the distinctly basic character of ethylene oxide, that the ethylenic oxide form of the hexose, not an enol, is the active agent. Assuming the enol to be concerned, acids equally with alkalis should convert one hexose into another in the Lobry de Bruyn change, but this is known not to be the case.

It is noteworthy, however, that ethylene oxide itself has no reducing power on either methylene-blue or indigo-blue in alkaline solution, although it readily affects permanganate. It is by no means clear, in fact, that the action of alkali is comparable with that of acid, and it may well be that reduction is effected by the enol. Whereas possibly in acid solution a salt of the basic ethylene oxide hexose is formed, in alkaline solution the scission of all ring systems and the production of a metallic salt of the open-chain enol appears more probable.

Whilst glucose decolorised the standard amount of permanganate initially in eleven minutes (in the presence of one equivalent of sodium hydroxide), fructose takes three and mannose twenty-five minutes; the figures after the solutions have remained for five hours are, respectively, glucose 3, fructose 1·25, and mannose 9 minutes.

As the formulæ show, all three substances can give the same enolic form. On the supposition that "enol" rather than "ethylene oxide" is initially formed in the presence of alkali, the configuration represented by fructose is most, and that represented

by mannose least, prone to undergo enolisation. This is in marked contrast to the behaviour of the same three sugars towards acid.



The change in presence of alkali is qualitatively proportionate to the strength of the alkali. It is of special interest in this connexion that pyridine has a similar effect to the other alkalis. In this case, as pyridine is such a weak alkali, the sugars were dissolved in the base itself. Decolorisation of glucose took place initially in about fifty to sixty minutes, increasing to thirty minutes in about five hours, whereas with fructose the times were thirty minutes initially and eight minutes after six hours.

This observation is quite in harmony with the important part which pyridine and quinoline have played in sugar chemistry as the media in which epimeric changes are effected, causing the rearrangement of the groups attached to the asymmetric carbon atom at the end of the chain. Both in the interconversion of epimeric hexonic acids (E. Fischer, *Ber.*, 1890, **23**, 2625) and of epimeric glucosides (E. Fischer and von Mechel, *Ber.*, 1916, **49**, 2813; 1917, **50**, 711), formation of intermediate modifications must be involved.

The alterations in structure which we have followed by the changes in reducing power are clearly in no way related to those known as mutarotation. Whereas the former take place instantaneously in the presence of acid, and more slowly in the presence of alkali, mutarotation is brought about immediately in the presence of alkali and more slowly in the presence of acid.

Experimental.

Reducing tests were made by withdrawing 10 c.c. of the sugar solution (generally 1 per cent., or 1/18 gram-molecule of hexose per litre, except when polarimetric comparisons were also made, in which case 5 per cent. solutions were used) into a stoppered test-tube and adding 2 c.c. of the standard permanganate or dye solution; *N*/100-potassium permanganate was invariably used, whilst

the dye solutions consisted respectively of a 0·025 per cent. solution of methylene-blue and a solution of neutral indigo sulphonates which contained 0·045 per cent. of indigotin. In those cases in which it was desired simultaneously to neutralise the acid or alkali present, special solutions of $N/100$-permanganate were employed containing respectively the amount of sodium hydroxide or of sulphuric acid per 2 c.c. necessary to neutralise the acid or alkali present in the 10 c.c. of sugar solution exactly.

The behaviour of permanganate with the sugar solutions varies considerably according to the conditions studied; thus, acid fructose or mannose solutions pass simply from pink to clear white, and perfectly definite end-points are obtainable in these cases. In other cases, generally those of slowly reducing acid media or of rapidly reducing neutral or alkaline solutions, the pink tint gives place, with varying rapidity, to a very pale yellow, and ultimately to the colourless, condition. A definite colour standard, just short of colourless, was adopted here, and sharp end-points could be obtained without difficulty. With slowly reducing neutral or weakly alkaline solutions, however, a precipitate of manganese dioxide of variable degree of fineness is apt to appear, and it is difficult to determine the precise point at which actual precipitation sets in; cases of this kind are denoted in the tables which follow by the addition of "indefinite" or "with pptn."

It is obvious that in the latter case the amount of reduction will not be so great as when the formation of the colourless manganous salt solution has occurred. In point of fact, whilst the 10 c.c. of sugar solution employed has contained 0·1 gram (1 per cent. solution) or 0·5 gram (5 per cent. solution) of hexose, the 2 c.c. of $N/100$-permanganate, assuming the action

$$C_6H_{12}O_6 + 2O = C_4H_5(OH)_4 \cdot CO_2H + H \cdot CO_2H$$

to occur, are capable of oxidising 0·0009 gram of hexose if the reduction proceeds to the manganous state, or 0·00054 gram if the action is arrested at the stage of manganese dioxide.

In the extreme cases, therefore, we have measured the time of oxidation of 0·9 per cent. of the sugar present in the solution, whilst, on the other hand, we have dealt with the time of oxidation of as small a proportion as 0·11 per cent. or less of the sugar present.

The stock solutions of sugars, and also the portions undergoing tests, were maintained at 25° throughout.

Neutral Solutions.

The dye reagents are unaffected by any of the sugars tested in neutral solution. Under the conditions described, permanganate is decolorised by fructose in four or five hours, whilst with either form of glucose the solution becomes orange in about six hours, and fades to a full yellow tint after twenty-four hours. The behaviour of mannose is very similar to that of glucose. These results are obtained equally with fresh solutions and those which have remained for a day at 25°.

It may be of interest to state that if the test is conducted in $N/10$-sodium chloride solution instead of in water, precipitation of manganese dioxide sets in at a much shorter time; the figures obtained for fructose, α-glucose, and mannose were respectively 93, 90, and 115 minutes.

Acid Solutions.

(i) *Aqueous Solutions.*—The oxidation times are constant at any age of the solution in the case of acids. This is illustrated by the figures for fructose, α- and β-glucose, and mannose given in table I.

The dependence of the time factor on the hydrion concentration is shown by the results in table II, wherein only the mean figures are quoted; it may be emphasised that the agreement of the individual readings at varying ages of the sugar solutions is in all cases as good as those given *in extenso* in table I.

Two series of times are given for each sugar, the first being for the simple acid solution; the second gives the values obtained when the test-solutions were neutralised simultaneously with the addition of permanganate.

In the case of the higher concentrations of hydrogen ions investigated, neutralisation of the acid present, effected at the same time as the addition of permanganate, does not appreciably alter the oxidation times.

At the lower concentrations of hydrogen ions, and notably with the weaker acids, such as phosphoric and acetic, the oxidation times for the "neutralised" solutions are quicker than for the acid solutions, and progressively so as the strength of the acid decreases.

The identity of the oxidation times for "neutralised" and for acid solutions with the stronger acid solutions is quite definite, and we consider that they indicate the persistence of the active form of the sugar after neutralisation of the acid has taken place; the meaning of the results with neutralised solutions of weaker acids is by no means clear, although they are explicable to a certain

extent when it is borne in mind that the sodium salts of the weaker acids will be appreciably hydrolysed, so that we have really passed over in this instance to a feebly alkaline solution of the sugar.

The age of the solution is given in hours, the first reading (0·1 hour) having been taken immediately solution was complete; in most instances, this reading was commenced about three to five minutes after the addition of acid. The times of oxidation are in minutes, unless an explicit statement to the contrary is added.

TABLE I.

One per cent. Sugars in $N/10$-HCl *and* $N/10$-H_2SO_4.

	Fructose.		α-Glucose.		β-Glucose.		Mannose.		
Age.	Acid.	Neutd.	Acid.	Neutd.	Acid.	Neutd.	Acid.	Neutd.	Acid.
0·1	17	15	29	27	30	30	13	12	HCl
1·0	16	17	28	29	32	30	12	13	
2·0	17	18	31	28	32	27	12	12	
5·0	16	18	29	—	34	29	12	17	
0·1	31	24	52	41	—	—	25	21	H_2SO_4
1·0	30	26	51	43	—	—	23	20	
2·0	28	22	51	42	—	—	22	20	
5·0	30	26	53	48	—	—	24	21	

TABLE II.

One per cent. Solutions of Fructose and α-Glucose in Acids of Varying Strength.

Acid.	Hydrion concentration. Equivs. per litre.	Fructose.		α-Glucose.	
		Acid.	Neutd.	Acid.	Neutd.
$N/10$-HCl	0·0910	16	17	29	28
$N/10$-H_2SO_4	0·0660	30	24	52	43
$N/50$-HCl	0·0188	69	62*	118	97*
$N/50$-H_2SO_4	0·0160	76	75*	124	75*
$N/10$-H_2PO_4	0·0130	211	84*	238	150*
$N/10$-$C_2H_4O_2$	0·0012	280	20*	1,070	65*

* With precipitation.

The hydrion concentrations are taken from data in Landolt and Börnstein's "Physikalische-Chemische Tabellen."

(ii) *Alcoholic Solutions.*—Some observations were made in methyl- and ethyl-alcoholic hydrogen chloride solutions in view of the considerable amount of synthetic work which has been carried out in these media. Concentrations of $N/20$-acid were employed in order to approximate to the 0·25 per cent. hydrogen chloride solutions which have most frequently been used by E. Fischer,

Irvine, and other workers with these reagents. Very similar results were obtained to those found in aqueous solutions.

The methyl alcohol was distilled over lime and then over a little fructose, whilst the ethyl alcohol was twice distilled over lime and potassium permanganate. Ten c.c. of the neutral solvents caused precipitation in the permanganate test in six hours in the case of methyl, and in sixteen hours with ethyl, alcohol. *N*/20-Methyl-alcoholic hydrogen chloride, however, decolorised the permanganate in ninety-eight minutes, the time with *N*/20-ethyl-alcoholic hydrogen chloride being fifty-six minutes.

TABLE III.

One per cent. Solutions of Fructose and α-Glucose in Alcoholic N/20-*Hydrogen Chloride.*

Solvent.	Age.	Fructose.	α-Glucose.
N/20-Methyl-alcoholic hydrogen chloride	0·1	7	11
	2·0	—	16
	3·0	17	—
	24·0	25	120
N/20-Ethyl-alcoholic hydrogen chloride	0·1	6	9
	2·0	7	20
	3·0	8	10
	24·0	6	23

Alkaline Solutions.

In alkaline solutions, it is also possible to utilise the reduction of the dyes indigo and methylene-blue; the former gives two fairly definite colour stages, passing from blue through green to a clear red, and then changing to pure yellow. The times occupied from the commencement of the test in reaching the standard red and yellow tints are given in the tables under the columns headed respectively "**R**" and "**Y**."

Methylene-blue fades to a colourless solution. In both cases, the dyes are restored by contact with air, and it was found desirable to fill the upper part of the test-tubes with an inert gas, hydrogen being employed.

It was found that the stock alkaline sugar solutions, whether maintained under air or under hydrogen, behaved the same towards the three oxidising agents.

The result of neutralising the alkaline sugar solution, when the latter has been freshly prepared, is to cause a very marked retard-

ation in reducing power, but after the alkaline solution has remained for some hours, the reducing power after neutralisation becomes greater, approaching that of the alkaline solution itself in about twenty-four hours.

This shows that initially the change induced by alkali is reversed on neutralisation, but the progressive alteration in behaviour is somewhat obscure, although it may well be due to the appearance of small amounts of decomposition products resulting from more profound disturbance of the sugar molecule.

It is evident, however, that the behaviour of neutralised alkaline solutions is quite distinct from that of neutralised acid solutions, so that it may be considered that the cause of the reducing activity of the sugar is not the same in each case.

The subjoined tables give the full series of readings up to five hours for fructose, α- and β-glucose, and mannose in the presence of one and of two equivalents of sodium hydroxide (table IV). In table V are recorded the initial and final values (five hours) for fructose and α-glucose with varying concentrations of sodium hydroxide, and in table VI we quote similar data for these sugars in the presence of one equivalent of a number of aqueous alkalis.

Correlation of the Reducing Action of the Sugars with Alterations in Optical Rotatory Power.

In order to obtain a convenient polarimetric reading in the 2-dcm. tubes employed, the behaviour of 5 per cent. solutions of fructose and of α-glucose was examined in neutral, acid, and alkaline media. The concentrations of the acid (N/10-HCl) and of the alkali (N/18-NaOH), and the conditions of the reducing time-tests, were otherwise maintained unaltered. The alteration in concentration of the sugars involved the determination of the corresponding times of reaction with permanganate and the dyes, and the results of these and of the observations of optical rotatory power are collected in table VII.

TABLE IV.

One per cent. Sugar Solutions with One and Two Equivalents of Aqueous Sodium Hydroxide.

(a) *Tests with Potassium Permanganate.*

NaOH equiv.	Age.	Fructose. Alk.	Fructose. Neutd.	α-Glucose. Alk.	α-Glucose. Neutd.	β-Glucose. Alk.	β-Glucose. Neutd.	Mannose. Alk.	Mannose. Neutd.
2·0	0·1	1·75	65·0*	10·0	61·0*	—	—	26	65†
	1·0	1·25	60·0*	8·0	90·0†	—	—	24	120†
	3·5	0·75	8·0	3·0	150·0†	—	—	16	150†
	5·0	0·50	0·5	2·0	60·0†	—	—	14	70
	24·0	0·75	0·2	1·75	1·25	—	—	7	13
1·0	0·1	3·00	60·0†	11·0	180·0†	15·0	35·0†	25	90†
	1·0	2·00	—	7·5	—	11·0	50·0†	20	—
	3·0	1·75	65·0	4·5	73·0*	9·0	48·0	17	73*
	5·0	1·25	11·0	3·0	48·0*	4·0	37·0	9	46*
	24·0	1·25	0·25	2·5	2·5	4·5	4·5	4	5

(b) *Tests with Indigo and Methylene-blue.*

NaOH equiv.	Age.	Fructose. Indigo. R.	Fructose. Indigo. Y.	Fructose. Meth. Blue.	α-Glucose. Indigo. R.	α-Glucose. Indigo. Y.	α-Glucose. Meth. Blue.	β-Glucose. Indigo. R.	β-Glucose. Indigo. Y.	β-Glucose. Meth. Blue.	Mannose. Indigo. R.	Mannose. Indigo. Y.	Mannose. Meth. Blue.
2·0	0·1	1·00	2·50	1·50	4·00	6·00	7·00	—	—	—	17†	21	29
	1·0	0·75	1·25	0·50	3·25	5·50	4·00	—	—	—	12†	18	21
	3·0	0·50	1·00	0·40	2·50	5·00	3·00	—	—	—	8†	15	11
	5·0	0·50	1·25	0·35	2·25	5·00	2·25	—	—	—	7†	15	10
	24·0	1·25	3·00	2·00	2·50	5·00	3·00	—	—	—	5†	10	6
1·0	0·1	2·25	3·50	3·00	9·0	12·5	11·0	14	19	18	22†	33	37
	1·0	1·50	2·75	1·25	6·5	11·5	7·0	8	15	12	19†	30	31
	3·0	1·25	2·50	1·00	6·0	11·5	5·0	7	14	9	16†	28	24
	5·0	1·25	2·50	1·00	5·0	11·0	4·0	5	11	5	17†	28	22
	24·0	3·25	4·75	2·00	5·0	9·0	5·5	4	7	4	17†	22	24

* Precipitation set in. † Indefinite end-point.

TABLE V.

One per cent. Solutions of Fructose and α-Glucose with Varying Strengths of Sodium Hydroxide.

			Fructose.					α-Glucose.				
			Indigo.			Permanganate		Indigo.			Permanganate.	
NaOH equiv.	OH ion concn. per litre.	Age.	R.	Y.	Meth. Blue.	Alk.	Neutd.	R.	Y.	Meth. Blue.	Alk.	Neutd.
2·0	0·0978	0·1	1·00	2·50	1·50	1·75	65·0*	4·00	6·00	7·00	10·0	61*
—	—	5·0	0·50	1·25	0·35	0·50	0·5	2·25	5·00	2·25	2·0	60†
1·0	0·0506	0·1	2·25	3·50	3·00	3·00	60·0†	9·0	12·5	11·0	11·0	180†
—	—	5·0	1·25	2·50	1·00	1·25	11·0	5·0	11·0	4·0	3·0	48*
0·75	0·0383	0·1	5·0	7·5	5·0	5·0	55·0*	14·0	21·5	19·5	16·0	57*
—	—	5·0	1·25	3·0	1·0	1·5	24·0	6·0	13·0	6·0	8·5	23*
0·5	0·0256	0·1	6·0	8·5	6·0	7·0	29·0*	20·0†	35·0	27·0	24·0	43*
—	—	5·0	3·0	4·5	3·0	3·5	19·0†	14·0†	23·0	19·0	15·0	36*
0·25	0·0129	0·1	15·0†	20·0	17·5	14·0	50·0*	51·0†	91·0	66·0	95·0†	50*
—	—	5·0	7·0†	10·0	5·0	5·0	51·0†	25·0†	50·0	25·0	33·0	31*

* Precipitation set in.

† Indefinite end-point.

TABLE VI.

One per cent. Solutions of Fructose and α-Glucose with One Equivalent of Various Alkalis.

			Fructose.					α-Glucose.				
			Indigo.			Permanganate.		Indigo.			Permanganate.	
Alkali.	OH ion concn. per litre	Age.	R.	Y.	Meth. Blue.	Alk.	Neutd.	R.	Y.	Meth. Blue.	Alk.	Neutd.
NaOH	0·0506	0·1	2·25	3·50	3·00	3·00	60†	9·0	12·5	11·0	11·0	180†
	—	5·0	1·25	2·50	1·00	1·25	11	5·0	11·0	4·0	3·0	48†
KOH	0·0506	0·1	4·50	6·00	5·00	4·00	120†	13·0	20·0	18·0	16·0	20*
	—	5·0	0·75	2·50	0·75	1·25	60	5·0	10·0	6·0	5·0	60
$Ba(OH)_2$	0·0478	0·1	5·00	6·00	5·00	4·00	—	15·0†	19·0	18·0	16·0	—
	—	5·0	1·00	1·50	1·25	1·25	—	4·0	6·5	5·0	4·0	—
Na_2CO_3	0·0024	0·1	†	83·0	150·0	30·0†	61*		Practically		95·0†	52*
(Hydrolysis)		5·0	†	56·0	98·0	16·0	20*		unchanged.		75·0†	31*
K_2CO_3	?	0·1	†	57·0†	88·0†	42·0†	39*		Practically		65·0*	39*
(Hydrolysis)		5·0	†	49·0†	60·0	27·0	27*		unchanged.		130·0†	24*
NH_4OH	0·0011	0·1		Very little		70·0	19*		Practically		150·0†	31*
	—	5·0		action.		48·0	60†		unchanged.		Indef.	40*

* Precipitation set in.

† Indefinite end-point.

TABLE VII.

Comparison of Rotatory Power with reducing Action of Sugars in 5 per cent. Solution.

(a) *Neutral Solutions.*

Age in hours.	Fructose. Permanganate.		$[\alpha]_D$.	Glucose. Permanganate.		$[\alpha]_D$.	β-Glucose. Permanganate.		$[\alpha]_D$.
0·1	24 hours.	Almost colourless	−104·2°	23 hours.	Still yellow	+96·8°	6 hours.	Almost colourless	+27·5°
0·5	—	—	92·5	—	—	—	—	—	33·8
1·0	24 hours.	Almost colourless	91·5	22 hours.	Still yellow	68·2	6 hours.	Pale yellow	37·8
2·0	24 hours.	„ „	91·2	—	—	—	—	—	44·5
3·0	—	—	—	—	—	—	—	—	—
3·5	—	—	—	22 hours.	Still yellow	52·0	—		—
4·0	—	—	91·2	—	—	—	20 hours.	Clear.	49·2
5·0	—	—	—	—	—	51·5	—	—	49·2
6·0	—	—	91·2	—	—	—	—	—	49·0
24·0	48 hours.	Almost colourless	91·2	Clear before 24 hours.		50·7	Clear before 24 hours.		49·5

TABLE VII. (*continued*).

(b) *Solutions in* N/10-*Hydrochloric Acid.*

Age in hours.	Fructose. Permanganate. Acid.	Fructose. Permanganate. Neutd.	Fructose. $[\alpha]_D$.	Glucose. Permanganate. Acid.	Glucose. Permanganate. Neutd.	Glucose. $[\alpha]_D$.	β-Glucose. Permanganate. Acid.	β-Glucose. Permanganate. Neutd.	β-Glucose. $[\alpha]_D$.
0·1	8	8	−91·2°	21	21	+91·8°	13	16	+30·5°
0·5	—	—	91·5	—	—	—	—	—	43·5
1·0	8	6½	91·5	21	20	51·2	13	14	49·8
2·0	7	6½	91·0	—	—	—	—	—	—
3·0	—	—	—	—	—	—	12½	29	49·5
3·5	—	—	—	18	20	49·8	—	—	—
4·0	7½	8	91·0	—	—	—	—	—	49·5
5·0	—	—	—	17	16½	49·8	13	25	49·5
6·0	—	—	90·8	—	—	—	—	—	—
24·0	8	10	90·8	20	14	49·8	14	29	49·5

TABLE VII. (*continued*).

(c) *Solutions in* N/18-*Sodium Hydroxide.*

	Fructose.						Glucose.						β-Glucose.					
	Indigo.			Permanganate.			Indigo.			Permanganate.			Indigo.			Permanganate.		
Age in hours.	R.	Y.	Meth. Blue.	Alk.	Neutd.	$[\alpha]_D$.	R.	Y.	Meth. Blue.	Alk.	Neutd.	$[\alpha]_D$.	R.	Y.	Meth. Blue.	Alk.	Neutd.	$[\alpha]_D$.
0·1	2·0	3·5	3·0	3·0	21	−89·7°	12	17½	15½	15½	30	+48·2°	19	24	23	18	64 indef.	+49·2°
0·5	—	—	—	—	—	89·2	—	—	—	—	—	—	—	—	—	—	—	46·7
1·0	1·75	3·5	1·5	2·5	16	88·0	9	14	12	13	25	46·7	9	15	13	9	40	46·0
2·0	1·75	2·5	1·5	2·0	15	86·7	—	—	—	—	—	—	—	—	—	—	—	—
3·0	—	—	—	—	—	—	5	11	7	7	16½	45·2	6½	11	8	6½	35	—
4·0	1·25	1·75	1·25	1·5	14½	84·2	—	—	—	—	—	—	—	—	—	—	—	44·2
5·0	—	—	—	—	—	—	3	6	4	4	15	42·5	6	11	6½	6	35	42·5
6·0	1·0	1·5	1·0	1·5	9½	83·3	—	—	—	—	—	—	—	—	—	—	—	—
24·0	1·75	2·25	2·0	1·5	1·0	81·5	3	7½	5	5	4	34·5	5	11	7½	8	6	39·2
Age in days.																		
2	—	—	—	—	—	—	—	—	—	—	—	30·2	—	—	—	—	—	33·0
4	—	—	—	—	—	49·5	—	—	—	—	—	23·2	—	—	—	—	—	23·5
8	—	—	—	—	—	—	—	—	—	—	—	10·0	—	—	—	—	—	10·0
12	—	—	—	—	—	—	—	—	—	—	—	+3·8	—	—	—	—	—	+6·7
25	—	—	—	—	—	−4·2	—	—	—	—	—	—	—	—	—	—	—	—

One per cent. Solutions of Fructose and Glucose in Pyridine.

In view of the interest attaching to the action of pyridine on the sugars, a few experiments were made with solutions of the two sugars in pure pyridine at 25°.

The pyridine was twice distilled over lime before use and boiled at 116—116·5°. Ten c.c. of the distilled pyridine caused no alteration in the blue tint of indigo or of methylene-blue (2 c.c. of the standard dye solutions) in twenty-four hours, but with 2 c.c. of *N*/100-permanganate a precipitate appeared in three hours.

The 1 per cent. fructose and glucose solutions in pyridine were also without action on the dyes, but results analogous to those of the weaker alkalis were obtained with permanganate. These are given in table VIII, in which the age of the solutions is in hours and the decolorisation times in minutes, as usual.

TABLE VIII.

One per cent. Solutions of Fructose and of α-Glucose in Pyridine.

Age.	Fructose.	α-Glucose.
0·1	30 not quite colourless	56 with very fine precipitation.
1·0	23 " "	40 " " " "
2·0	17 " "	
3·5		35 " " " "
4·2	12 " "	
5·0		30 " " " "
6·0	8 " "	

Comparative Experiments with Simple Aldehydes and Derivatives of Ethylene Oxide.

Some experiments were made on the reducing action of aqueous solutions of acetaldehyde, *n*-butaldehyde, acetone, and epichlorohydrin and ethylene oxide. In neutral 1/18th gram-molecular solution all these substances, with the exception of acetone, caused the pink colour of the permanganate in our standard test to disappear within about two hours, but the resulting clear orange solution underwent no further change in colour for many hours. In the case of acetone, the pink tint did not entirely vanish for several hours.

The results of the permanganate tests in *N*/10-hydrochloric acid solution are given in the next table; in the case of ethylene oxide, the exact concentrations were not accurately known, but tests were made with two strengths, approximately gram-molecular per litre and 1/18th gram-molecular per litre.

Table IX.

Solutions of Aldehydes and of Ethylene Oxides in N/10-*Hydrochloric Acid.*

Substance.	Concn. per litre.	Age.	Permanganate tests. Acid.	Neutralised.
Acetaldehyde ...	*M*/18	0·1	6½ hrs. Pale yellow	9 minutes, with pptn.
		1·0	6½ hrs. „ „	7 „ „
		3·0	2 hrs. „ „	10 „ „
n-Butaldehyde ...	*M*/18	0·1	3½ hrs. Pale yellow	13 minutes, with pptn.
		1·0	2½ hrs. „ „	10 „ „
		3·5	2½ hrs. „ „	10 „ „
		24·0	2½ hrs. „ „	10 „ „
Epichlorohydrin	*M*/18	0·1	140 minutes.	82 minutes.
		1·5	120 „	53 „
		4·3	90 „	35 „
		24·0	120 „	32 „
Ethylene oxide ...	*M*/18	0·1	103 minutes.	80 minutes.
		1·0	132 „	89 „
		3·0	130 „	80 „
		23·0	110 „	20 „
	M	0·1	8 minutes.	10 minutes.
		1·0	12 „	13 „
		2·0	17 „	14 „
		5·0	16 „	14 „
		23·0	15 „	14 „

Table X illustrates the data obtained in *N*/18-aqueous sodium hydroxide; with both aldehydes, acetone, and epichlorohydrin and ethylene oxide, indigo passed rapidly through green to a pale yellow colour, and the original blue tint could not be restored by shaking the yellow solution with air. It appears, therefore, that some action was proceeding in these cases beyond simple reduction to indigo-white, and the colour test is not valid in this instance.

Table X.

Solutions of Aldehydes and of Ethylene Oxides in N/18-*Sodium Hydroxide.*

Substance.	Concn. per litre.	Age.	Methylene-blue.	Permanganate. Alkaline.	Neutralised.
Acetaldehyde	*M*/18	0·1	60†	11*	11*
		1·0	32†	6*	50
		3·5	21†	16*	30
		5·0	23†	16*	18
		23·0	35†	6*	1

* Precipitation set in. † Indefinite end-point.

TABLE X. (*continued*).

Solutions of Aldehydes and of Ethylene Oxides in N/18-*Sodium Hydroxide.*

Substance.	Concn. per litre.	Age.	Methylene-blue.	Permanganate. Alkaline.	Permanganate. Neutralised.
n-Butaldehyde.....	*M*/18	0·1	39†	8*	8*
		1·0	20	5*	8*
		3·5	14	7*	7*
		5·0	12	8*	8
		23·0	13	19*	2
Acetone.....	*M*/18	0·1	Permanent.	Pale green, then turbid yellow.	In 16 hours, precipitation, but still pink.
		1·3			
		3·3			
		5·3			
		23·0			
Epichlorohydrin	*M*/18	0·1	Permanent.	113*	207
		1·5	,,	100*	140
		4·3	,,	95*	116
		24·0	,,	80*	110
Ethylene oxide	*M*/18	0·1	Permanent.	245†	352
		1·0	,,	236†	350
		3·0	,,	220†	340
		23·0	,,	174†	320
	M	0·1	Permanent.	76†	87
		1·0	,,	77†	84
		2·0	,,	71	88
		5·0	,,	55	77
		23·0	,,	19*	53

* Precipitation set in. † Indefinite end-point.

The most interesting points in this series of experiments are:

(i) The alkaline solutions of the aldehydes reduce methylene-blue similarly to the sugars, and there is some similarity in their behaviour to alkaline permanganate.

(ii) The ethylene oxide derivatives show no similarity to the sugars in alkaline solution, either with respect to permanganate or to methylene-blue.

(iii) On the other hand, the acid solutions of the ethylene oxide compounds display great likeness to those of acid sugar solutions, both in the "acid" and "neutralised" permanganate tests.

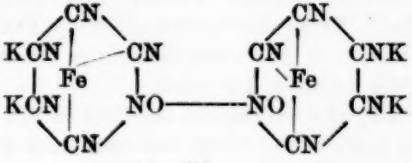
WARRINGTON. [*Received, November 13th*, 1919.]

CXXXIV.—*The Constitution of the Nitroprussides. Part I. Conductivity and Cryoscopic Measurements.*

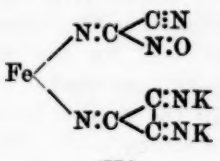
By George Joseph Burrows and Eustace Ebenezer Turner.

From time to time, the nitroprussides have been made the subject of considerable speculation, but little attempt has been made to verify experimentally the various constitutions assigned to them.

Hofmann, who is responsible for most of the experimental work in this field (*Annalen*, 1900, **312**, 1), assigned to sodium nitroprusside the co-ordination formula $[Fe(CN)_5NO]Na_2$. Friend (T., 1916, **109**, 721), apparently without further experimental work, proposed for potassium nitroprusside the formula (I).



(I.)



(II.)

This formula corresponds with the empirical one given in works of reference (for example, Moissan, "Traité de chimie minérale," 1905, 417), which formula, however, seems never to have had any evidence in its favour.

Friend at the same time rejected the formula (II) suggested by Browning (T., 1900, **77**, 1238) for potassium nitroprusside, in view of his theory as to the constitution of the ferrocyanides, which theory has since been shown to be unnecessary (Bennett, T., 1917, **111**, 490).

It was suggested by one of us (T., 1916, **109**, 1130) that a determination of the molecular weights of some nitroprussides would throw light on the problem, and, as a result, a number of nitroprussides have been prepared and investigated cryoscopically and their conductivities measured. From the results so obtained, the number of ions present in a solution of a nitroprusside has been calculated, and conclusions have been drawn as to the molecular weights of the salts in question. In these experiments, the degree of dissociation of the salt at any particular dilution was found in the usual way by dividing the molecular conductivity at that dilution by its value at infinite dilution. From cryoscopic measurements, the molecular depression of the freezing point of water was found for various concentrations of the salt, and by dividing this number by 18·7 (the molecular constant for water), the value for

i (the van't Hoff coefficient) was obtained. The number of ions, k, into which each molecule of the salt dissociates was then obtained by substituting the experimental values of a and i in the equation

$$i=1+(k-1)a.$$

A similar method was used by Petersen (*Zeitsch. physikal. Chem.*, 1902, **39**, 249) in connexion with the cobaltammines. This author was of the opinion that the conclusions drawn by Werner (*Zeitsch. physikal. Chem.*, 1893, **12**, 35, etc.) from measurements of the molecular conductivity at a dilution of 1000 litres (not necessarily at infinite dilution) were in most cases inaccurate.

The figures given by Jones (*Carnegie Institute of Washington, Publication* No. 170) for the molecular conductivities of a large number of salts show that most salts are completely dissociated at dilutions of about 1000 litres. In some cases, however, the molecular conductivity again increases beyond that dilution, owing to causes other than dissociation. From the figures given by Petersen (*loc. cit.*) for the conductivity of the cobaltammines, it would appear that similar difficulties arose in his work.

In the present investigation, the substances considered are salts of a strong acid. (This has been found to be the case from a preliminary examination of the molecular conductivity of nitroprussic acid itself.) The conductivities of the salts were determined for solutions diluted to 2048 litres, and the values were plotted against the concentrations. The value for infinite dilution was found by extrapolation from the curve so obtained. In all cases, the value of μ_∞ differs only slightly from the value actually found for μ_{1024}, a result which was expected from the nature of the salts in question.

In the following tables are given the values of k calculated on the assumption that the nitroprussides are represented by the simple formula $M_2'[Fe(CN)_5NO]$, which will be referred to in future as type I. In addition, the value of k_1 has been calculated in each case for a molecule, $M_4'[Fe_2(CN)_{10}(NO)_2]$ (type II).

In the case of a univalent cation, a molecule of type I will dissociate into three ions, type II giving five ions. The value of k should therefore approximate to 3 if formula I is correct, whilst if II is correct, $k_1=5$. In the same way, a salt of a bivalent cation should give the values $k=2$ or $k_1=3$.

It is considered that the results obtained show conclusively that all the nitroprussides examined conform to the simple formula (type I). They are salts of $H_2[Fe(CN)_5NO]$, and not of

$$H_4[Fe_2(CN)_{10}(NO)_2].$$

The possible effect due to hydration of the ions has not been overlooked (compare Jones, *Carnegie Institute of Washington, Publi-*

cation No. 180), and it is considered that the conclusions drawn from the figures obtained in the present work cannot be regarded as vitiated on this ground. Whereas hydrate formation may account for the differences between the experimental and absolute values of k, the extremely large differences in the case of k_1 cannot be accounted for in this way.

It is hoped in a future communication to describe the alkyl nitroprussides, some of which have been prepared, although in an impure state only.

Experimental.

The conductivity measurements were all made at 25·0°. The degree of dissociation of salts at 0° differs only slightly from that at 25°, and the latter temperature allows of greater accuracy in determining the conductivity. In the following tables, v is the number of litres containing one gram-molecule of the salt (calculated for the simple formula I), μ is the molecular conductivity, a is the degree of dissociation and is equal to μ_v/μ_∞, Δ_t is the observed depression of the freezing point of water, $M\Delta_t$ is the molecular depression and is equal to $v \times \Delta_t \times 10$, i is the van't Hoff coefficient and is equal to $M\Delta_t/18{\cdot}7$, and k is the number of ions into which a molecule dissociates, and is obtained from the equation $i=1+(k-1)a$; k_1 is the corresponding value of k calculated for a molecule of type II by doubling i and then substituting in the equation $i=1+(k_1-1)a$.

The values of a in the cryoscopic tables are taken from the curves obtained from conductivity data.

Sodium Nitroprusside, $Na_2[Fe(CN)_5NO],2H_2O$.

The salt used was a pure specimen.

Conductivity Measurements.

v.	μ.	a.
4	155·2	0·63
8	169·4	0·69
16	181·8	0·74
32	194·3	0·79
64	204·9	0·84
128	214·2	0·87
256	222·0	0·91
512	229·2	0·94
1024	236·2	0·96
2048	244·6	—
∞	245·0	—

Cryoscopic Measurements.

v	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
47·1	0·115	54·1	2·90	0·81	3·35	6·9
24·4	0·218	53·2	2·84	0·77	3·40	7·1
14·55	0·345	50·2	2·68	0·73	3·30	7·0
10·81	0·456	49·3	2·64	0·71	3·30	7·0
8·76	0·560	49·1	2·62	0·70	3·31	7·0
7·12	0·678	48·3	2·58	0·68	3·32	7·1

Type I requires $k=3$. Type II requires $k_1=5$.

Potassium Nitroprusside, $K_2[Fe(CN)_5NO]$.

This salt was prepared by decomposing the barium salt with the calculated weight of pure potassium sulphate, filtering off the barium sulphate, and evaporating the filtrate at a low temperature under diminished pressure. The residue so obtained was crystallised from aqueous alcohol containing about 95 per cent. of alcohol. It crystallises in pale pink crystals without water of crystallisation:

0·4010 gave 0·1076 Fe_2O_3. Fe = 18·8.

$C_5ON_6FeK_2$ requires Fe = 19·0 per cent.

Conductivity Measurements.

v.	μ.	a.
8	199·2	0·745
16	205·2	0·795
32	215·7	0·836
64	227·2	0·881
128	236·6	0·917
256	244·0	0·946
512	249·3	0·966
1024	257·0	0·996
2048	258·1	—
∞	258·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
34·4	0·150	51·6	2·76	0·85	3·07	6·32
24·1	0·213	51·3	2·74	0·82	3·12	6·46
14·66	0·316	46·3	2·48	0·79	2·87	6·01
11·65	0·405	47·2	2·52	0·77	3·00	6·25
7·02	0·641	45·0	2·41	0·74	2·91	6·16
4·78	0·909	43·4	2·32	0·71	2·86	6·11

Type I requires $k=3$. Type II requires $k_1=5$.

Barium Nitroprusside, $Ba[Fe(CN)_5NO],3H_2O$.

This salt was prepared by precipitating a solution of the sodium salt with zinc sulphate and boiling the zinc salt so obtained with a suspension of precipitated barium carbonate. The filtered solution of the barium salt was evaporated under diminished pressure

at a low temperature, and the salt crystallised from aqueous alcohol:

0·8344 gave 0·4734 $BaSO_4$. Ba = 33·4.

$C_5ON_6BaFe,3H_2O$ requires Ba = 33·7 per cent.

The anhydrous salt was found to be extremely hygroscopic.

Conductivity Measurements.

v.	μ.	α.
8	152·9	0·63
16	165·9	0·68
32	177·1	0·73
64	190·7	0·79
128	203·0	0·84
256	216·2	0·89
512	223·6	0·92
1024	236·9	0·98
2048	240·5	—
∞	243·0	—

Cryoscopic Measurements.

v.	Δ_f.	$M\Delta_f$.	i.	$\alpha=\mu_v/\mu_\infty$.	k.	k_1.
37·7	0·093	35·1	1·88	0·74	2·19	4·73
16·5	0·180	29·7	1·59	0·68	1·87	4·21
9·87	0·285	28·1	1·50	0·64	1·78	4·13
6·67	0·413	27·6	1·47	0·61	1·77	4·18
4·73	0·575	27·2	1·45	0·59	1·76	4·22

Type I requires $k=2$. Type II requires $k_1=3$.

This salt is of especial interest, owing to the rough equality in weights of the anion and cation.

Ammonium Nitroprusside, $(NH_4)_2[Fe(CN)_5NO]$.

This salt was obtained by decomposing the barium salt with an equivalent weight of ammonium sulphate, filtering, evaporating under diminished pressure, and crystallising from aqueous alcohol, when reddish plates, very readily soluble in water, were obtained:

0·2390 gave 0·0768 Fe_2O_3. Fe = 22·5.

$C_5ON_6Fe(NH_4)_2$ requires Fe = 22·2 per cent.

Conductivity Measurements.

v.	μ.	α.
16	206·7	0·77
32	218·0	0·82
64	228·5	0·85
128	236·7	0·89
256	245·6	0·92
512	251·2	0·94
1024	261·3	0·98
2048	266·2	—
∞	268·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$\alpha=\mu_v/\mu_\infty$.	k.	k_1.
26·3	0·214	56·4	3·01	0·80	3·51	7·27
10·73	0·450	48·3	2·58	0·74	3·14	6·62
6·68	0·704	47·0	2·51	0·69	3·19	6·83

Type I requires $k=3$. Type II requires $k_1=5$.

Methylammonium Nitroprusside, $(MeNH_3)_2[Fe(CN)_5NO]$.

This salt and the nitroprussides of di- and tri-methylamine were obtained by treating a solution of the free acid (obtained from the barium salt and the calculated sulphuric acid) with a slight excess of an alcoholic solution of the amine. The solution so obtained was evaporated under diminished pressure, and the solid residue crystallised from alcohol. The alkylammonium nitroprussides crystallise in reddish plates, which are very readily soluble in water. In appearance they resemble the barium or ammonium salts:

0·1117 gave 0·0306 Fe_2O_3. Fe = 19·2.
$C_5ON_6Fe(MeNH_3)_2$ requires Fe = 20·0 per cent.

Conductivity Measurements.

v.	μ.	α.
32	185·2	0·77
64	197·7	0·82
128	208·0	0·87
256	218·5	0·91
512	225·8	0·94
1024	233·4	0·97
∞	240·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$\alpha=\mu_v/\mu_\infty$.	k.	k_1.
36·6	0·148	54·2	2·90	0·78	3·45	7·2
19·05	0·262	49·9	2·67	0·71	3·35	7·1
14·15	0·339	48·0	2·57	0·68	3·31	7·1
10·13	0·466	47·2	2·52	0·62	3·45	7·5
8·35	0·541	45·2	2·42	0·59	3·41	7·5

Type I requires $k=3$. Type II requires $k_1=5$.

Dimethylammonium Nitroprusside, $(Me_2NH_2)_2[Fe(CN)_5NO]$.

0·1028 gave 0·0272 Fe_2O_3. Fe = 18·5.
$C_5ON_6Fe(Me_2NH_2)_2$ requires Fe = 18·1 per cent.

Conductivity Measurements.

v.	μ.	a.
16	156·5	0·68
32	172·1	0·75
64	185·2	0·81
128	196·3	0·85
256	205·8	0·90
512	212·5	0·92
1024	220·2	0·96
2048	227·3	—
	230·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
35·2	0·149	52·4	2·80	0·76	3·37	7·05
16·4	0·294	48·1	2·57	0·68	3·31	7·09
8·84	0·500	44·2	2·36	0·61	3·23	7·10
5·92	0·714	42·3	2·26	0·57	3·21	7·20

Type I requires $k=3$. Type II requires $k_1=5$.

Trimethylammonium Nitroprusside, $(Me_3NH)_2[Fe(CN)_5NO]$.

0·2234 gave 0·0512 Fe_2O_3. Fe = 16·0.

$C_5ON_6Fe(Me_3NH)_2$ requires Fe = 16·7 per cent.

Conductivity Measurements.

v.	μ.	a.
16	137·1	0·65
32	154·0	0·73
64	167·3	0·80
128	183·0	0·86
256	191·7	0·90
512	201·1	0·95
1024	208·0	0·98
2048	210·5	—
∞	212·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
39·0	0·134	52·2	2·79	0·75	3·39	7·11
14·47	0·290	42·0	2·24	0·63	2·97	6·52
6·56	0·588	38·6	2·06	0·50	3·12	7·24

Type I requires $k=3$. Type II requires $k_1=5$.

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CXXXV.—*The Propagation of Flame in Complex Gaseous Mixtures. Part I. Limit Mixtures and the Uniform Movement of Flame in such Mixtures.*

By WILLIAM PAYMAN.

IN order that flame may propagate through a mixture of an inflammable gas with air or oxygen, the heat developed by a given "layer" on burning must be sufficient to raise the contiguous layer of unburnt gas to its ignition temperature. In a "limit mixture" there is just sufficient, and only just sufficient, heat developed to accomplish this. If limit mixtures of two or more inflammable gases be mixed together, this heat balance should remain unaltered provided that all of the limit mixtures are of the same kind, that is to say, all lower-limit or all upper-limit mixtures. It follows that all mixtures, in any proportions, of limit mixtures should remain limit mixtures, the limiting percentage being that of the mixed inflammable gas. Conversely, any limit mixture of a complex inflammable gas will consist of a number of limit mixtures of the individual gases it contains.

Assuming this reasoning to be correct, imagine a limit mixture with air of a complex inflammable gas. Let A, B, C, . . . be the simple constituents of this inflammable gas, and their limits of inflammability, N_A, N_B, N_C, . . . respectively. Suppose also that the complex limit mixture contains a per cent. of A, b per cent. of B, c per cent. of C, . . . Then this limit mixture will contain

$$aA + bB + cC + \ldots + [100 - (a + b + c + \ldots)] \text{ air.}$$

This limit mixture, *ex hypothesi*, comprises a series of limit mixtures of the simple inflammable gases. In such a simple limit mixture of A, for example, every N_A parts of A are associated with $100 - N_A$ parts of air, so that every a parts of A are associated with $\left(\frac{100 - N_A}{N_A}\right)a$ parts of air. Similarly, for B, C, . . .

The complex limit mixture will therefore contain

$$a + \left(\frac{100 - N_A}{N_A}\right)a, \qquad b + \left(\frac{100 - N_B}{N_B}\right)b, \qquad c + \left(\frac{100 - N_C}{N_C}\right)c, \ldots$$

Since these terms are expressed as percentages, they will together equal 100, so that

$$a + \left(\frac{100 - N_A}{N_A}\right)a + b + \left(\frac{100 - N_B}{N_B}\right)b + c + \left(\frac{100 - N_C}{N_C}\right)c + \ldots = 100.$$

This expression, on simplification, becomes

$$\frac{a}{N_A} + \frac{b}{N_B} + \frac{c}{N_C} + \ldots = 1.$$

This is the formula of Le Chatelier, which has been shown to apply accurately for both the upper and lower limits of inflammability of a number of complex gaseous mixtures with air (Coward, Carpenter, and Payman, this vol., p. 27).

This "formula," but not the generalisation from which it has been deduced, applies only to mixtures of inflammable gases with an atmosphere of constant composition, such as air. For the numerical quantities involved in the formula relate to the combustible gases only, and admit of no allowance being made for variations in the proportions of inert gas present. The generalisation, however, should hold good for all limit mixtures; for mixtures in which the proportion of inert gas is greater or less than in air, or even in which its proportion is not constant.*

The effect of an inert gas (nitrogen) on the limits of inflammability of methane has been investigated by Burgess and Wheeler (T., 1914, **105**, 2596), who determined the limits for this gas in several artificial atmospheres of oxygen and nitrogen containing less oxygen than air. During the course of the present inquiry into the mode of combustion of mixed gases, it became necessary to extend their work to include atmospheres containing more oxygen than air, and pure oxygen.

The method of experiment used by Burgess and Wheeler, which involved the central ignition of the mixtures in a large globe, was not employed in the present research. This investigation is mainly concerned with the uniform movement of flame, and the determinations of the limits were made in the same apparatus as was used for measuring the speed of propagation of flame. This consisted of a horizontal glass tube 2·5 cm. in diameter, open at one end and closed at the other, the mixtures being ignited close to the open end of the tube by means of an electric spark. The criterion of inflammability was, therefore, the horizontal propagation of flame throughout the length of the tube.

The determinations were carried out by the method of trial and error, using mixtures which differed in composition by about 0·10 per cent. of methane. Throughout this paper, the term "limit mixture," whether upper or lower, implies that mixture in which flame was just able to propagate.

The results of the determinations are given in table I. The limits were always sharply defined. On sparking a mixture con-

* This will be described in future as the "limits generalisation."

taining a little less than the lower-limit percentage of inflammable gas, there usually arose a ball of flame which travelled some 5 or 6 cm. along the tube. A mixture containing slightly more inflammable gas than the higher-limit percentage usually produced a flame which travelled the short distance from the spark to the open end of the tube, owing to the dilution of the mixture there by diffusion of the outside air. In the limit mixtures, flame travelled steadily and at an approximately uniform speed throughout the length of the tube.

In no instance did the flame of the burning limit mixture fill the whole cross-section of the tube, but it was usually similar to the trailing flames described by Burgess and Wheeler (T., 1914, **105**, 2593). This was most marked with the upper-limit mixtures and with the lower-limit mixture of methane in pure oxygen. These flames were about 10 mm. in diameter and about 15 mm. long, and had a short tail, resembling a "Prince Rupert's drop" in shape.

In three instances the deposition of carbon was noticed during the passage of flame through a limit mixture, namely, in the upper-limit mixtures of methane with atmospheres containing 50, 66, and 100 per cent. of oxygen.* The flames resembled that of a tallow candle, and the odour of the residual gases was similar to that caused by the smouldering wick of such a candle. In general, the upper-limit flames were olive-green in colour. The colour of the lower-limit flames was pale blue.

TABLE I.

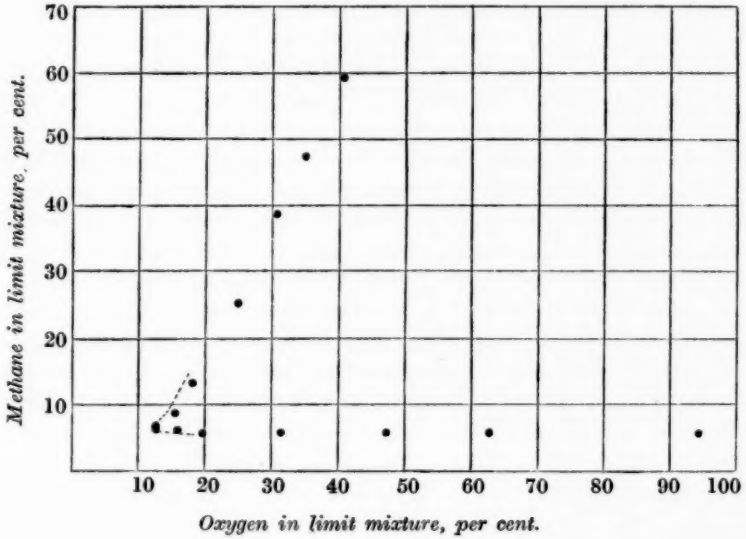
The Limits of Inflammability of Methane in Mixtures of Oxygen and Nitrogen.

Percentage of oxygen in atmosphere.	Percentage composition of limit mixtures. Lower limit. CH_4.	O_2.	N_2.	Upper limit. CH_4.	O_2.	N_2.
13·7	6·4	12·8	80·8	6·9	12·7	80·4
17·0	6·1	16·0	77·9	8·9	15·5	75·6
21·0 (air)	5·8	19·8	74·4	13·3	18·2	68·5
33·0	5·8	31·4	62·8	25·1	25·0	49·9
50·0	5·8	47·1	47·1	38·8	30·6	30·6
66·0	5·8	62·8	31·4	47·5	35·0	17·5
100·0	5·7	94·2	—	59·2	40·8	—

* According to Bone (*Phil. Trans.*, 1915, **215**, 275), when methane and oxygen mixtures are exploded under pressure, "there is a total cessation of any separation of carbon (which is very marked with mixtures $2CH_4 + O_2$) after the proportion of oxygen in the original mixture exceeds the limit $3CH_4 + 2O_2$." No carbon was deposited when a mixture containing 59·3 per

The results are plotted in the diagram, the ordinates representing percentages of methane and the abscissæ percentages of oxygen in the limit mixtures.

If the "limits of generalisation" given earlier in this paper applies to these mixtures, the values for each of the two sets of limits should lie on a straight line. It will be seen that this holds accurately over a large range of mixtures, namely, over those containing more than about 17 per cent. of oxygen.* Mixtures containing less than this amount of oxygen require rather more methane than the theoretical quantities to attain both the upper and lower limits.



The dotted lines in the diagram represent the values obtained by Burgess and Wheeler (*loc. cit.*). The shapes of both curves are

cent. of methane and 40·7 per cent. of oxygen was exploded under a pressure of 12·7 atmospheres.

In the present series of experiments, at atmospheric pressure, a mixture of approximately the same composition as that used by Bone (59·2 per cent. of methane and 40·8 per cent. of oxygen) deposited carbon, as did also mixtures containing less oxygen in proportion to the methane present, namely, those intermediate in composition between $3CH_4+2O_2$ and CH_4+O_2. It would therefore appear that the limiting composition at which the deposition of carbon ceases is not fixed, but varies with the initial pressure of the mixture.

* According to Burgess and Wheeler (*loc. cit.*), no mixture of methane, oxygen, and nitrogen is capable of propagating flame when there is less than about 13 per cent. of oxygen present.

similar, the difference in magnitude being due to the difference in experimental conditions.

Little change was observed in the lower limit until the mixtures contained a large excess of nitrogen; whilst the value with pure oxygen was only slightly lower than that with air. The latter observation is not in agreement with the results recorded by Parker (T., 1914, **105**, 1002), who found the lower limit of inflammability of methane to be slightly higher with oxygen than with air (6·0 per cent. and 5·8 per cent. respectively). The apparatus used by Parker was similar to that previously used by Burgess and Wheeler, namely, a 2-litre globe in which the mixtures were ignited at the centre.

This lack of agreement is undoubtedly due to the difference in the position of the point of ignition in the two sets of experiments. It has frequently been noted that the limits of inflammability vary with the position of the point of ignition according as the flame has to pass upwards or downwards through the gas mixture. The fact that a flame will pass more readily upwards than downwards is well illustrated when a lower-limit mixture of methane in air, for example, is ignited by a spark at the centre of a globe. As soon as the spark passes, a flame shoots to the top of the vessel, bends over, and then moves slowly downwards to the bottom.

In order to investigate this point further, a series of experiments was carried out to determine quantitatively the effect of varying the point of ignition on the limits of inflammability of methane in air and in oxygen. A glass tube 2·5 cm. in diameter was used, closed at one end and fitted with firing points at the other (open) end.

TABLE II.

Limits of Inflammability of Methane with Different Positions of the Point of Ignition.

	Percentage of methane in lower-limit mixture.	
Mode of propagation.	Air.	Oxygen.
Upward	5·5	5·4
Horizontal	5·9	5·8
Downward	6·1	6·3
Central ignition (Parker)...	5·8	6·0

Both for upward and horizontal propagation the lower limit of inflammability of methane is less in oxygen than in air. For downward propagation, however, the order is reversed. The differences observed are not very great, although too large to be accounted for by experimental error. Of the factors which determine the value of the limiting percentage of inflammable gas, the

transference of heat by convection and the absorption of heat by the mixture may be mutually opposed. During the downward propagation of flame, convection does not materially affect the transference of heat to unburnt layers of the mixture; the influence of the slightly higher specific heat of oxygen as compared with that of nitrogen therefore becomes apparent. With horizontal and upward propagation of flame, however, the influence of convection currents masks the effect of the higher specific heat of oxygen.

The change of order of the results, dependent on the direction of travel of the flame, is more marked when the results for methane in air are compared with those for hydrogen. Such a comparison is made in table III.

TABLE III.

Lower Limits of Inflammability in Air of Methane and of Hydrogen.

	Percentage of inflammable gas	
Mode of propagation.	Methane.	Hydrogen.
Upward	5·5	4·2
Horizontal	5·9	6·2
Downward	6·1	9·7
Central ignition	5·8	9·2

Attempts have been made to calculate the limits of inflammability of a gas from its thermal constants. It will be clear from a consideration of the results recorded in table III that any such calculation is doomed to failure unless allowance can be made for the influence of convection currents.

Since the lower limit of inflammability of methane (downward propagation of flame) is less with air than with oxygen, it might be expected to be less still with an atmosphere containing less oxygen than air. This, however, is not so. The lower limit of inflammability of methane in an atmosphere containing 17 per cent. of oxygen was found to be 6·3 per cent. for downward propagation of flame. This limit is thus affected in the same sense as both limits for horizontal propagation in mixtures containing only a small percentage of oxygen; that is to say, more methane is required to form the limit mixture than would be expected from results with mixtures richer in oxygen.

This displacement of the range of inflammability corresponds with the displacement of the range for maximum speed of uniform movement of flame in mixtures of methane and air. It has been generally assumed that the latter displacement is due to the higher thermal conductivity of methane as compared with that of air. A

similar displacement is found, however, when the inflammable gas has a thermal conductivity less than that of air, as will be shown in a subsequent communication. The displacement under consideration in the present paper, and other similar displacements, have one feature in common, namely, that the mixtures contain a large proportion of inert gas (nitrogen), together with only a slight excess of one or other of the reacting gases above the quantity required for complete combustion.

A possible explanation of the results is that the mode of combustion in such mixtures differs from that in mixtures containing a large excess of either of the reacting gases. Such an explanation is supported by the analyses of the "flame gases" recorded by Burgess and Wheeler in the paper to which reference has already been made. The samples of gas were rapidly snatched from the flames in such a manner as to cool the primary products of combustion before secondary reactions could come into play. It will be seen on examining the table of analyses (p. 2604) that all mixtures containing less than 15 per cent. of oxygen appear to be influenced by the deficiency of reacting gas (whether methane or oxygen), and it is in these mixtures that the generalisation regarding limiting percentages no longer holds. With the upper-limit mixtures of low oxygen content, the primary products of combustion contain smaller quantities of hydrogen than of carbon monoxide, whereas with the higher-limit mixtures containing a greater proportion of oxygen, the quantities of hydrogen and carbon monoxide produced are equal.

Similarly with the lower-limit mixtures of low oxygen content, the primary products of combustion contain more carbon monoxide than hydrogen, whilst with lower-limit mixtures containing more than 15 per cent. of oxygen these gases are absent altogether from the products of combustion. Further consideration of these results is reserved for a future communication, as is also the consideration of the displacement of the range for maximum speed of uniform movement of flame in mixtures of air with inflammable gases.

The Uniform Movement of Flame in Limit Mixtures.

The speed of horizontal propagation of flame in the limit mixtures in a tube 2·5 cm. in diameter was determined by the method described by Wheeler (T., 1914, **105**, 2606). The results are given in table IV.

TABLE IV.

Speed of Propagation of Flame in Limit Mixtures of Methane, Oxygen, and Nitrogen in a Tube 2·5 cm. in Diameter.

Percentage of oxygen in atmosphere.	Speed in cm. per sec.	
	Lower limit.	Upper limit.
13·7	21·9	19·1
17·0	22·4	19·0
21·0 (air)	23·3	19·1
33·0	23·0	18·9
50·0	22·8	18·9
66·0	21·3	19·4
100·0	19·9	18·9

The upper-limit speeds are identical within the range of experimental error. The speeds in the lower-limit mixtures are throughout slightly higher than the corresponding upper-limit speeds, although with pure oxygen the difference is very small. A noticeable feature of these flames, common to them all, was their small size in comparison with the diameter of the tube. This was more marked with the flames in the upper-limit than in the lower-limit mixtures, a fact which no doubt accounts for the slower speed of the former flames. For the smaller the flame, the greater is its surface in proportion to its volume, and the greater in proportion is the transference of heat from the flame to the walls of the tube. If this explanation be correct, it follows that the speeds of flames in limit mixtures should increase with increased diameter of the tube in which they travel. This was found to be so by Mason and Wheeler (T., 1917, **111**, 1052).

With tubes of very small diameter, on the other hand, the speed of flame at the limits is comparatively high (Payman and Wheeler, T., 1918, **113**, 656), but for another reason. With such tubes, the cooling effect of the walls is so great as to have a marked effect on the value of the limits, the range of inflammability of the mixtures rapidly narrowing as the diameter of the tube is diminished. Moreover, convection currents have no appreciable influence in tubes of such small diameter.

It seemed probable that the speed of flame in a limit mixture, determined under standard conditions, should approach a constant value irrespective of the nature of the inflammable gas. To test this, the speeds of flame have been determined in limit mixtures of air with several of the paraffin hydrocarbons. The results are given in table V, which is of value also in recording the limits of inflammability (horizontal propagation of flame).

The limits differ slightly from those found (central ignition in

a large globe) by Burgess and Wheeler, whose results are inserted in the table in brackets.

In the upper-limit mixtures the flames vibrated rapidly about half-way along the tube, and were sometimes extinguished there. The difference between a limit mixture and one which could only propagate flame for a short distance, if at all, was, however, well marked.

TABLE V.

Limits of Inflammability and Limiting Speeds of Flame in Mixtures of Air with the Paraffin Hydrocarbons in a Tube 2·5 cm. in Diameter.

	Lower limit.		Upper limit.	
Hydrocarbon.	Per cent. of combustible.	Speed, cm. per sec.	Per cent. of combustible.	Speed, cm. per sec.
Methane, CH_4	5·8 (5·6)	23·3	13·3 (14·8)	19·1
Ethane, C_2H_6	3·3 (3·4)	18·1	10·6 (10·7)	19·7
Propane, C_3H_8	2·4 (2·3)	20·8	7·3 (7·3)	20·3
Butane, C_4H_{14}	1·9 (1·6)	20·1	6·5 (5·7)	20·3
Pentane, C_5H_{12}	1·6 (1·4)	20·2	5·4 (4·5)	20·2
($CH_4 + C_5H_{12}$*)	2·6 (2·5)†	22·3	7·7 (7·7)†	20·7

* Equimolecular mixture of methane and pentane.

† Calculated from values for methane and pentane.

The "limit speed" is thus found to approach a constant value, as foreshadowed by Burgess and Wheeler (T., 1914, **105**, 2596), not only with each of the paraffin hydrocarbons singly, but also with the mixture of methane and pentane. There is no reason to doubt but that the limit speed of flame would have the same value for any mixture of the paraffins.

The speeds of flame in limit mixtures with air of carbon monoxide and hydrogen have also been determined. With carbon monoxide, the speed at both limits (in a tube 2·5 cm. in diameter) is 19·4 cm. per second, which agrees well with the speeds for the paraffins. With hydrogen, the speed at the lower limit is remarkably slow, namely, 10 cm. per second. The flame is exceedingly small, consisting of a tiny ball of flame, which, however, travels the full length of the tube. For reasons given in a previous communication (this vol., p. 41), it was not found possible to determine accurately the speed of flame in the upper-limit mixture of hydrogen and air.

The equimolecular mixture of methane and pentane corresponds with propane in percentage composition and calorific value, and yields the same products on complete combustion. The marked difference between the limits of inflammability of the mixed gases and those of propane shows that these are not the only factors on which the limits of inflammability depend. Similarly, a mixture

of three volumes of pentane and two volumes of hydrogen corresponds with propane, but this mixture of gases has limits 2·5 (lower) and 8·6 (upper) as compared with propane, 2·4 and 7·3.

These differences are perhaps due to the ability of the constituents of the mixed inflammable gases to burn independently. This subject will be dealt with more fully in succeeding papers of this series.

Experimental.

The speeds of propagation of flame in limit mixtures were determined in glass tubes by the method described by Wheeler (T., 1914, **105**, 2610). Two tubes were employed, both 2·5 cm. in diameter; one, 3 metres long, used for the majority of the experiments; the other, used for the mixtures with atmospheres rich in oxygen, was only 1·5 metres long, so as to avoid the setting up of the detonation wave, with consequent shattering of the tube.

The platinum firing points were about 2 cm. from the open ends of the tubes. At measured distances along each tube were fused ground-glass tubulures, which carried glass plugs with stout platinum wires fused through them. Fine "screen wires" of copper were stretched across these platinum supports inside the tube, and electrical connexion was established with an automatic commutator and chronograph by means of platinum terminals on the outside of the plugs.

In order to fill the tubes with the mixture required for experiment, they were exhausted of air by means of an oil-pump, half filled with the mixture, and re-exhausted before being finally filled. A sample of the gas was then taken for analysis.

The limits of inflammability for upward and downward propagation of flame were determined in a similar tube 1·5 metres long, but without side-pieces.

The gases were prepared in the usual manner, the paraffin hydrocarbons being purified by repeated liquefaction and subsequent fractional distillation until, on explosion of a sample with excess of air and oxygen, the theoretical value for the ratio C/A was obtained.

The methane used in the limit determinations in pure oxygen contained 99·8 per cent. of CH_4, and the ratio C/A was found to be 2·00. The oxygen was prepared by gently heating recrystallised potassium permanganate, and contained 99·6 per cent. of O_2.

The gases were stored over water rendered alkaline by potassium hydroxide, and the mixtures were therefore saturated with water vapour.

Eskmeals,
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CXXXVI.—*The Propagation of Flame in Complex Gaseous Mixtures. Part II. The Uniform Movement of Flame in Mixtures of Air with the Paraffin Hydrocarbons.*

By William Payman.

In the preceding paper it was shown that all mixtures of limit mixtures are themselves limit mixtures. With each of the paraffin hydrocarbons, the speed of the uniform movement of flame at the limits tends to a constant value under standard conditions of experiment. The same speed was found with all limit mixtures of methane, oxygen and nitrogen, and with an equimolecular mixture of methane and pentane at its limits with air. There is no reason to doubt that the same speed would be obtained with all mixtures of the paraffin hydrocarbons at the limits.

The generalisation advanced in the previous paper was thus shown to apply to all such mixtures. The question immediately arises whether what is true of the speeds of flames at the limits holds also for other speeds. Whether, for example, given two or more mixtures of air with different individual gases, in each of which the speed of flame was the same, all combinations of the mixtures would propagate flame at the same speed. Should this be so, a simple method would be available for the calculation of the speed of propagation of flame in complex gaseous mixtures from the known values for the simple constituent gases. Such a calculation could naturally only apply over the whole range of mixtures when the maximum speed of flame in mixtures of the several individual gases with air was the same; otherwise calculation would be restricted to such mixtures as possessed a speed of flame not greater than the lowest of the individual maximum speeds. It is clear, also, that the mixtures taken for the purpose of calculation must be all of the same nature; that is to say, must all contain excess of combustible gas, or must all contain excess of oxygen.

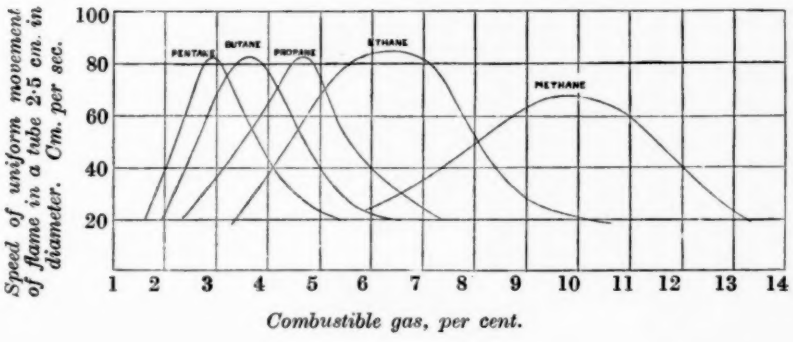
The mixtures of the paraffin hydrocarbons with air seemed most suitable to determine whether the generalisation that applies to speeds of flames at the limits is capable of extension to the speeds of the uniform movement over the whole range of inflammable mixtures.

Measurements were therefore made of the speed of the uniform movement in mixtures of air with each one of the hydrocarbons of the paraffin series up to and including pentane. The determinations were carried out as described in the previous paper, in a

horizontal glass tube 2·5 cm. in diameter and 3 metres long. The results are recorded in table I. The majority of the values in column 1 for methane were obtained by Mason and Wheeler (T., 1917, **111**, 1052).

The results are shown diagrammatically in Fig. 1. With the exception of methane, the maximum speeds are approximately the same, namely, about 82 cm. per second. The value for methane is rather lower than this, being 67 cm. per second. Owing to the few data available for the thermal constants of the paraffin hydrocarbons, it is not easy to explain this difference. In each instance, the mixture having the maximum speed of flame contains more combustible gas than is required for complete combustion.

FIG. 1.



For testing the application of the generalisation * to speeds other than the limiting speeds, the gases methane and pentane were first chosen, since they were both readily obtainable in ample quantity. Two air mixtures were prepared, one containing 7·35 per cent. of methane and the other 1·98 per cent. of pentane. In these two mixtures the speed of the uniform movement is the same, about 40 cm. per second (twice the speed at the limits), and they both contain excess of oxygen. The mixtures were then combined in varying proportions, and the speeds of the uniform movement determined in the usual manner. The results are recorded in table II.

* This may be termed the "speed generalisation."

Table I.

Speed of Uniform Movement of Flame in Mixtures of Air with the Paraffin Hydrocarbons in a Horizontal Glass Tube 2·5 cm. in Diameter.

Methane.		Ethane.		Propane.		Butane.		Pentane.	
Per cent. of combustible.	Speed, cm. per sec.	Per cent. of combustible.	Speed, cm. per sec.	Per cent. of combustible.	Speed, cm. per sec.	Per cent. of combustible.	Speed, cm. per sec.	Per cent. of combustible.	Speed, cm. per sec.
5·71	Ball of flame to 15 cm. from spark.	3·16	Flare of flame only.	2·30	Flame to 6 cm. from spark.	1·90	Flame to 6 cm. from spark.	1·52	Flame to 6 cm. from spark.
5·80	23·3	3·30	18·1	2·37	20·8	1·95	20·1	1·61	20·2
6·06	26·2	3·58	25·6	2·58	26·0	2·05	23·3	1·98	40·1
6·28	28·0	4·47	52·7	2·80	31·4	2·57	49·1	2·35	60·2
6·95	35·0	4·90	65·0	3·50	48·2	3·01	67·9	2·63	74·3
7·10	37·0	5·57	80·5	4·28	72·8	3·40	80·2	2·92	83·0
7·47	42·0	6·08	82·5	4·39	79·1	3·66	82·6	3·00	82·1
7·82	47·4	6·53	85·6	4·71	82·1	4·05	75·0	3·13	76·0
8·58	58·0	7·07	81·3	4·84	80·2	4·34	61·9	3·35	65·9
9·12	64·4	7·38	75·7	5·14	66·0	4·88	43·4	3·49	61·5
9·52	66·6	7·70	60·4	5·90	41·2	5·50	27·7	3·85	48·0
9·96	66·2	8·23	45·8	6·58	30·2	6·27	22·0	4·00	44·0
10·32	65·5	9·00	27·7	7·10	23·0	6·53	20·3	4·32	33·0
10·64	63·5	9·50	23·1	7·30	20·3	6·60	Flame to open end only.	4·56	28·7
11·10	57·0	10·09	20·8	7·35	Flame to 15 cm. from spark.			4·87	25·8
11·63	47·4	10·60	19·7					5·40	20·2
12·25	35·0	10·71	Flame to 4 cm. from spark.					5·50	Flame to open end only.
12·55	30·5								
13·09	22·0								
13·35	19·1								
13·42	Flame to 5 cm. from spark.								

TABLE II.

Speeds of Uniform Movement of Flame in a Glass Tube 2·5 cm. in Diameter with Mixtures containing 7·35 per cent. of Methane and 1·98 per cent. of Pentane, respectively, Mixed Together.

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed, cm. per sec.
100·0	—	39·3
75·0	25·0	39·2
50·0	50·0	39·6
25·0	75·0	39·9
21·2	78·8	39·2*
—	100·0	40·1

* Methane and pentane in equimolecular proportions.

It will be seen that the speeds are identical within the limits of experimental error.

Two mixtures containing excess of combustible gas, with speeds further removed from that at the limits, were then examined in the same manner. These mixtures contained 11·00 per cent. of methane and 3·54 per cent. of pentane, respectively, and the speed of the uniform movement of flame in them was about 60 cm. per second, three times the value at the limits. The results are given in table III.

TABLE III.

Speeds of Uniform Movement of Flame in a Glass Tube 2·5 cm. in Diameter with Mixtures containing 11·00 per cent. of Methane and 3·54 per cent. of Pentane, respectively, Mixed Together.

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed, cm. per sec.
100·0	—	59·1
75·0	25·0	59·1
50·0	50·0	60·3
25·0	75·0	59·1
24·4	75·6	59·1*
—	100·0	59·6

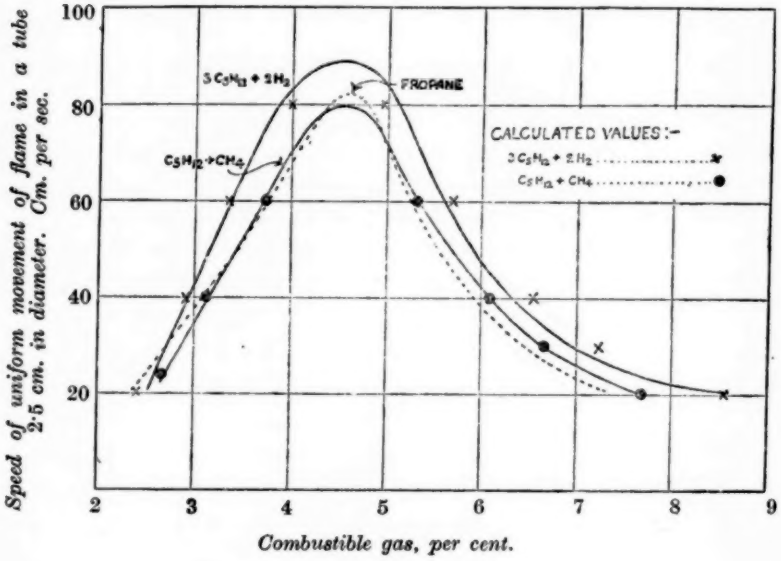
* Methane and pentane in equimolecular proportions.

Once more the generalisation is found to hold with great accuracy, and there is no doubt that it is true for all mixtures of the paraffins having the same speeds of flame provided that the maximum speed in mixtures of any individual paraffin with air is not too nearly approached. For if the generalisation could be supposed to apply to the "maximum-speed" mixtures, no mixture of air containing both methane and pentane should propagate the

uniform movement of flame at a speed higher than the maximum speed in mixtures of methane and air. Similarly, the generalisation cannot apply to speeds at the limits in mixtures of methane with atmospheres containing a high proportion of nitrogen, for with such atmospheres both upper and lower limits of inflammability lie at the maximum, flattened portion of the speed–percentage curve.

Bearing these limitations in mind, it should be possible to calculate the values for the speed–percentage curve for any combination of the paraffins in air. An equimolecular mixture of methane and

FIG. 2.



pentane (which corresponds with propane) was chosen to test the accuracy of such calculations.

The results are recorded in table IV, and are compared with the calculated values in Fig. 2. In no instance was the difference between observed and calculated speeds greater than 1 cm. per second. The highest speed for which calculation was made was 60 cm. per second.

It must be admitted that the gases chosen for these experiments are particularly favourable towards the calculation, since the maximum speed of the uniform movement is nearly the same with each gas. As a more stringent test, a mixture of pentane and hydrogen was prepared ($3C_5H_{12} + 2H_2$, corresponding with propane), and a

series of speed determinations and calculations made as before. In this instance, the maximum speeds of uniform movement in mixtures of the individual gases with air differ widely, being 82 cm. per second for pentane and 485 cm. per second for hydrogen. The results are recorded in table IV, and in Fig. 2 are compared with those calculated.

TABLE IV.

Speed of Uniform Movement of Flame in Mixtures of Air with Combinations of Gases corresponding with Propane in a Glass Tube 2·5 cm. in Diameter.

(*a*) $CH_4 + C_5H_{12}$.		(*b*) $3C_5H_{12} + 2H_2$.	
Combustible gas. Per cent.	Speed, cm. per sec.	Combustible gas. Per cent.	Speed, cm. per sec.
2·55	6 cm. travel only	2·35	Cap only
2·65	22·3	2·47	19·7
3·12	39·2	3·02	43·3
3·54	53·7	3·56	67·7
4·04	70·7	4·03	82·7
4·52	78·3	4·48	89·5
5·05	73·6	4·91	83·7
5·36	59·1	5·77	54·0
6·23	37·5	6·25	43·6
7·03	25·4	7·10	27·9
7·70	20·7	7·80	23·1
7·79	3 cm. travel only	8·60	21·5
		8·72	15 cm. travel

The results are not in as good agreement with calculation as those obtained with the combination of methane and pentane, but, even so, the agreement is remarkably close considering the wide difference between the individual maximum speeds of flames. The greatest difference between observed and calculated results is only 4 cm. per second. The highest speed for which calculation was made was 60 cm. per second, which is rather close to the maximum speed for pentane.

It will no doubt be apparent that a limit is at present set to the scope of the generalisation, because only the speeds of flames in mixtures with air are available for purposes of calculation. When it is remembered that the gas with the slower maximum speed of uniform movement of flame may have that maximum greatly enhanced if an atmosphere richer in oxygen than air is used, it is clear that the generalisation should be capable of further extension, given the necessary experimental data. The consideration of this subject is reserved for a later paper.

It now remains to deduce a method for calculating the maximum speed of the uniform movement of flame in a mixture of air with a mixture of inflammable gases, and also for calculating the com-

position of the mixture which will have this maximum speed of flame. The latter may be calculated by the method suggested in a previous communication (Payman and Wheeler, this vol., p. 36), in which it was shown that if "maximum-speed" mixtures were mixed together, the result would be the "maximum-speed" mixture for the mixed inflammable gases. For example, the value for the maximum speed of uniform movement of flame for hydrogen is 38·5 per cent., for pentane 2·9 per cent., and for methane 9·9 per cent.* The calculated value for the equimolecular methane–pentane mixture is 4·48 per cent., and for the pentane–hydrogen mixture ($3C_5H_{12}+2H_2$) 4·60 per cent. The value found is the same for both mixtures, namely, 4·55 per cent. It is interesting to note that the same value is found for propane, with which these mixed inflammable gases correspond.

It was also suggested, from a consideration of the results obtained with mixtures of air with an equimolecular mixture of methane and hydrogen, that the gas for which the maximum speed of flame was the lower had the predominating effect in determining what would be the maximum speed with mixed inflammable gases. This is true for mixtures of methane and hydrogen, but, in general, it is the gas requiring most air to attain the maximum speed of flame which is the deciding factor. This is, indeed, what one would expect from a consideration of the generalisation concerning the speeds in mixed gases. The larger the volume of air a combustible gas requires to produce its "maximum-speed mixture," the smaller is the percentage of that combustible gas in the fastest-speed mixture of air with a mixture of gases that contain it.

A method for calculating approximately the maximum speed of the uniform movement of flame in mixtures of air with a mixed inflammable gas, from the known values for its simple constituents, may be given from a consideration of this fact. The assumption is made that when "maximum-speed" mixtures are mixed together, the resulting speed is proportional to the amount of each mixture present and to the respective maximum speeds of their flames. This relationship, which holds roughly for mixtures with air, may be expressed as follows:

$$S = \frac{aS_a+bS_b+cS_c+\ \ldots\ .}{a+b+c\ \ldots\ .},$$

where S is the speed required; a, b, c, . . . are the amounts present of each maximum-speed mixture with air; S_a, S_b, S_c, . . . are the speeds of flame in those mixtures respectively.

The use of the formula will be best explained by an actual

* In each instance the figure given is the mean percentage over a range of mixtures having nearly the same speed.

calculation of the maximum speed of flame for the equimolecular mixture of methane and pentane in admixture with air.

The calculated value for the mixture to have the maximum speed of flame is 4·5 per cent., and this mixture will contain 2·25 per cent. each of methane and pentane. In the maximum-speed mixture of pentane and air, 100 parts of the mixture contain 2·9 parts of pentane, and therefore 2·25 parts of pentane correspond with $\frac{2{\cdot}25}{2{\cdot}9} \times 100 = 77$ parts of pentane–air mixture.

Similarly, 2·25 parts of methane correspond with 23 parts of methane–air mixture, since the maximum-speed mixture of methane and air contains 9·9 per cent. of methane.

Substituting these values in the above formula,

$$S = \frac{(77 \times 82) + (23 \times 67)}{100}$$
$$= 78{\cdot}5 \text{ cm. per second.}$$

The value found was 79 cm. per second, showing an extremely close agreement.

The agreement is not so good with the pentane–hydrogen mixture ($3C_5H_{12} + 2H_2$), the calculated value being 100 cm. per second and the speed found 90 cm. per second. The discrepancy does not appear so great, however, when it is remembered that there is a difference of 400 cm. per second between the maximum speeds of the flames in mixtures of pentane and air and hydrogen and air.

The maximum speed of flame with mixed gases and air may also be found by a graphical method. If on a speed–percentage graph the maxima for any two gases taken singly is joined by a straight line, all the maxima for mixtures of these two gases lie approximately on this line. The composition of the "maximum-speed" mixture is calculated by the method given by Payman and Wheeler (*loc. cit.*), and the speed then read off from the graph.

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CXXXVII.—*The Propagation of Flame in Complex Gaseous Mixtures. Part III. The Uniform Movement of Flame in Mixtures of Air with Mixtures of Methane, Hydrogen and Carbon Monoxide, and with Industrial Inflammable Gases.*

By William Payman.

The common industrial gases contain as their inflammable constituents methane, hydrogen, and carbon monoxide in various proportions.

The speed of the uniform movement of flame in mixtures of methane and air in a tube 2·5 cm. in diameter was given in Part II of this series of papers. The speeds with hydrogen and air in a similar tube (over the major portion of the range of inflammable mixtures) have been determined by Haward and Otagawa (T., 1916, **109**, 83). The speeds in mixtures of carbon monoxide and air are recorded in the present paper.

Mixtures of Carbon Monoxide and Air.—It is well known that the rate of combustion of carbon monoxide is dependent on the amount of water vapour present. Dixon, for example (*Phil. Trans.*, 1893, **184**, 97), has shown that the velocity of the detonation wave in a mixture of carbon monoxide and oxygen ($2CO + O_2$) increases with the percentage saturation of water vapour.

The present series of determinations of the speed of the uniform movement of flame in mixtures of carbon monoxide and air was carried out with mixtures saturated with water vapour at the ordinary temperature and pressure. Since the room temperature varied, it was not surprising to find that the speed in a given mixture did not remain constant from day to day. Identical results were, however, obtained in experiments made within a few minutes of each other at the same temperature and pressure. Table I illustrates the effect of change in the percentage saturation of water vapour on the speed of the uniform movement of flame in a mixture of carbon monoxide and air containing 50 per cent. of carbon monoxide.

Table I.

Speed of Uniform Movement of Flame in a Mixture of Carbon Monoxide and Air (50 *per cent.* CO) *in a Tube* 2·5 *cm. in Diameter.*

Temperature and pressure.	Cm. per sec.	
10° and 750 mm.	(1) 59·9	(2) 59·9
15° and 750 mm.	(1) 65·0	(2) 64·5
17° and 755 mm.	(1) 79·4	(2) 79·0

A series of determinations of speeds of flame over the whole range of inflammable mixtures was carried out during a period when the temperature of the laboratory did not alter appreciably (about 12°). The values obtained are given in table II.

TABLE II.

Speed of Uniform Movement of Flame in Mixtures of Carbon Monoxide and Air in a Tube 2·5 cm. in Diameter at 12° and 750 mm.

Per cent. of carbon monoxide.	Cm. per sec.	Per cent. of carbon monoxide.	Cm. per sec.
16·15	Tongue of flame only.	59·81	54·2
16·29	19·5	65·55	37·4
16·40	19·4	65·84	36·3
16·51	19·4	67·10	30·2
24·47	34·0	67·57	29·6
30·50	46·0	69·00	26·0
44·84	60·1	70·63	20·0
50·45	59·9	70·68	20·3
54·40	57·8	71·19	19·4
59·58	56·2	71·31	Trailing flame travelled 15 cm.

These values are of interest in themselves, apart from their connexion with the problem of the propagation of flame in complex gaseous mixtures, inasmuch as they disclose the fact that the maximum speed of flame is obtained with mixtures containing from 45 to 50 per cent. of carbon monoxide. The mixture for complete combustion contains 29·5 per cent. carbon monoxide, so that the "displacement" of the maximum-speed mixture is greater even than with hydrogen, despite the fact that the thermal conductivity of carbon monoxide is but little different from that of air.

Industrial gas mixtures may contain varying proportions of water vapour. There may therefore be some uncertainty as to the correct values to use for the speed of flame in mixtures of carbon monoxide and air when attempting to calculate the speed of flame in the mixed industrial gas. Such gases, however, contain hydrogen as well as carbon monoxide, and the presence of hydrogen affects the speed of flame in a similar degree to that of water vapour. With mixtures of gases containing fairly high proportions of hydrogen, it is therefore not unlikely that the effect of variation in the moisture content would be inappreciable. It should therefore be sufficient for our purpose to know the values for the speed of flame in mixtures of air with a mixture of hydrogen and carbon monoxide. Or the "effective" speeds for mixtures of carbon monoxide and air could be calculated from such values and these speeds used for further calculation.

In this connexion, it is interesting to note that Berthelot (*Ann. Chim. Phys.*, 1881, [v], **28**, 289) found the rate of detonation in mixtures of carbon monoxide and oxygen to be about half the calculated value. For mixtures of oxygen with carbon monoxide plus hydrogen, the calculated values were in good agreement with those found. Similarly, in the present research, the maximum speed of uniform movement of flame in mixtures of carbon monoxide and air is found to be about half the value calculated, making use of the values determined for hydrogen–air and hydrogen–carbon monoxide–air mixtures.

Mixtures of Hydrogen and Air.—As with tubes of smaller diameter (this vol., p. 36), it was not found possible to determine accurately the speed of the uniform movement of flame in the upper-limit mixture of hydrogen and air in a tube 2·5 cm. in diameter. A mixture containing 71·4 per cent. of hydrogen was found to be the richest which would propagate flame under the experimental conditions. The flame was not hot enough to melt "screen wires," but its speed, as measured by means of a tapping key in connexion with a chronograph, was found to be approximately 50 cm. per second.

A characteristic of the lower-limit mixture and of mixtures near to it is the formation on ignition of minute balls of flame, which pass steadily from the open to the closed end of the tube. These flames are propagated mainly by the influence of convection currents, and the speed–percentage curve at the lower-limit region is not continuous, but shows a definite break. Nevertheless, no definite distinction, at the point of break in the curve, could be drawn between the normal and the balls of flame, the latter increasing in size and gradually changing their form as the percentage of hydrogen increased.

The speeds of the flames in mixtures near the limits are given in table III, which completes the table given by Haward and

TABLE III.

Speed of the Uniform Movement of Flame in Mixtures of Hydrogen and Air in a Tube 2·5 cm. in Diameter.

Hydrogen. Per cent.	Speed, cm. per sec.
6·10	No flame observed.
6·19	10
6·31	12
6·52	15
14·71	120
71·39	50
71·51	Flame to open end only.

Otagawa (*loc. cit.*, p. 89). In only one instance was the flame hot enough to melt "screen wires," namely, with the mixture containing 14·71 per cent. of hydrogen; the remaining speeds were determined by means of a tapping key.

Mixtures of Methane, Hydrogen, and Air.—The speed of the uniform movement of flame in a tube 2·5 cm. in diameter was determined over a range of mixtures of air with two mixtures of methane and hydrogen. The first mixture contained equal volumes of methane and hydrogen ($CH_4 + H_2$), the second three volumes of methane to one volume of hydrogen ($3CH_4 + H_2$). The results are recorded in table IV. The lower-limit flames preserved the general character of the corresponding hydrogen flames, and their speeds were found to be lower than the speed in the limit mixture of methane and air.

TABLE IV.

Speed of the Uniform Movement of Flame in Mixtures of Air with Hydrogen Methane Mixtures in a Tube 2·5 cm. in Diameter.

$CH_4 + H_2$.		$3CH_4 + H_2$.	
Combustible gas. Per cent.	Speed, cm. per sec.	Combustible gas. Per cent.	Speed, cm. per sec.
6·03	15·0	6·09	18·0
6·20	17·1	6·22	19·9
6·31	19·1	6·50	21·0
6·73	22·1	6·80	27·7
7·68	28·6	7·84	39·6
9·05	45·6	9·06	58·3
10·23	67·4	9·93	78·7
11·95	104·1	11·35	84·9
11·99	106·3	12·26	82·2
13·50	128·6	13·25	66·7
14·93	135·3	14·20	45·7
15·93	127·3	14·99	27·8
16·90	111·9	15·50	22·6
18·31	65·6		
19·96	35·5		
20·22	30·5		
20·32	28·5		
20·48	27·3		
20·80	24·3		

The results are plotted as curves in Fig. 1, the calculated curves being shown in dotted line. The maximum speeds calculated by the method given in Part II are 150 and 99 cm. per second respectively for the mixtures $CH_4 + H_2$ and $3CH_4 + H_2$. The values found were 135 and 85 cm. per second.

Mixtures of Carbon Monoxide, Hydrogen, and Air.—Two mixtures of carbon monoxide and hydrogen were employed, of composition $CO + H_2$ and $3CO + H_2$, corresponding with the methane–hydrogen mixtures. The results are given in table V, and are plotted as curves in Fig. 2.

FIG. 1.

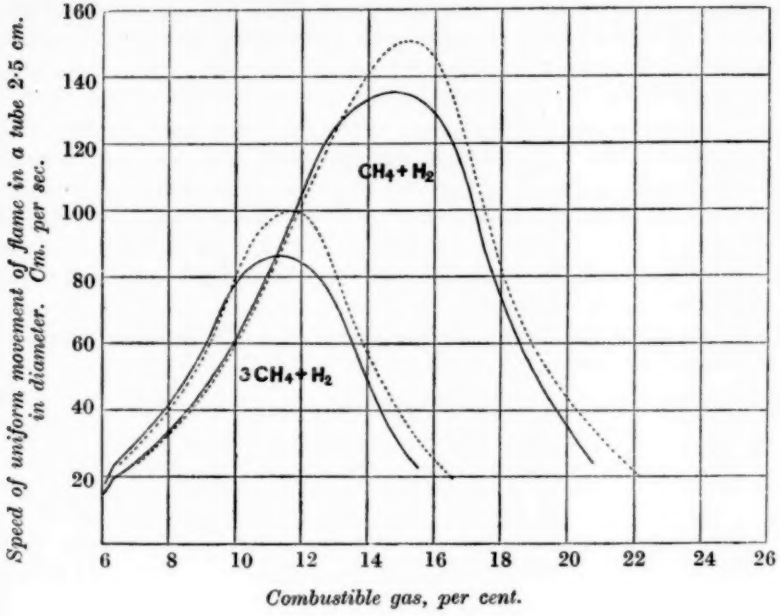
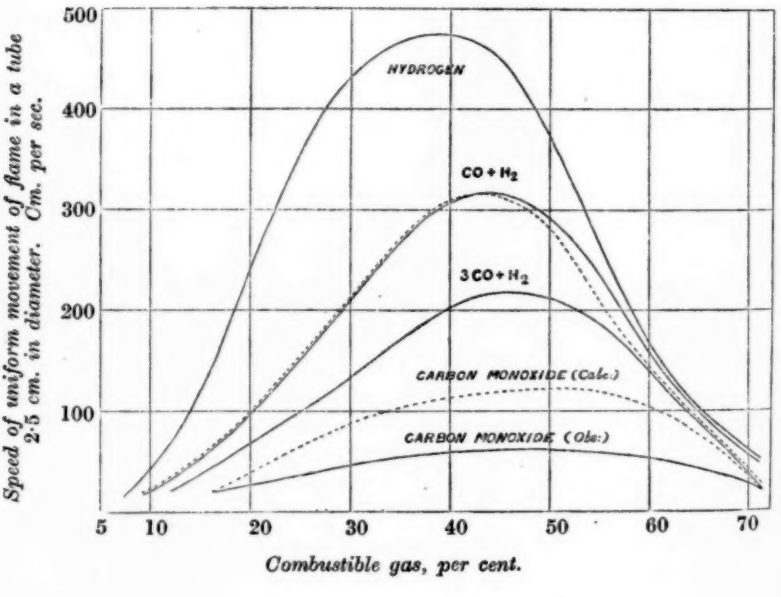

Speed of uniform movement of flame in a tube 2·5 cm. in diameter. Cm. per sec.
160
140
120
100
80
60
40
20
CH4 + H2
3CH4 + H2
6
8
10
12
14
16
18
20
22
24
26
Combustible gas, per cent.

FIG. 2.


Speed of uniform movement of flame in a tube 2·5 cm. in diameter. Cm. per sec.
500
400
300
200
100
HYDROGEN
CO + H2
3CO + H2
CARBON MONOXIDE (Calc.)
CARBON MONOXIDE (Obs.)
5
10
20
30
40
50
60
70
Combustible gas, per cent.

From the values found for hydrogen and for the mixture $3CO + H_2$, the speeds of the flames in mixtures of air with $CO + H_2$ were calculated. The results are shown in dotted line in Fig. 2. The values for carbon monoxide and air were also calculated from these values, and the curve is given in the diagram for comparison. It will be seen that the values calculated in this manner are much higher than those found by experiment. These "effective" speeds have been used in subsequent calculations instead of the values as determined, which are dependent on the amount of water vapour present.

TABLE V.

Speed of Uniform Movement of Flame in Mixtures of Air with the Mixtures $CO + H_2$ *and* $3CO + H_2$ *in a Tube 2·5 cm. in Diameter.*

$CO + H_2$.		$3CO + H_2$.	
Combustible gas. Per cent.	Speed, cm. per sec.	Combustible gas. Per cent.	Speed, cm. per sec.
9·25	18·2	12·00	19·2
10·35	21·1	18·99	67·1
15·40	58·3	27·82	115·0
20·57	100·4	34·73	166·2
30·25	211·5	41·32	205·5
36·94	282·9	46·90	214·0
41·50	309·7	53·17	200·0
45·92	315·2	58·49	154·7
51·23	280·0	70·36	34·4
58·55	178·5	71·42	20·8
69·00	64·5		
70·75	50·1		
71·34	44·4		

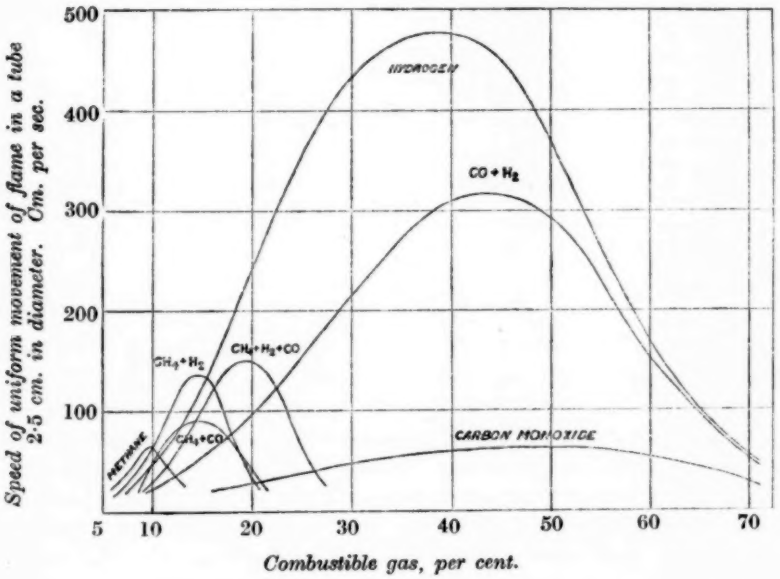
Mixtures of Methane and Carbon Monoxide, and Mixtures of Methane, Hydrogen, and Carbon Monoxide with Air.—Table VI records the results obtained with a mixture containing equal volumes of methane and carbon monoxide, and with one containing equal volumes of methane, hydrogen, and carbon monoxide. Methane, or any gas into the composition of which hydrogen enters, acts towards mixtures of carbon monoxide and air in a manner comparable with that of hydrogen and water vapour. The maximum speed of uniform movement of flame in mixtures of air with each of the mixtures $CH_4 + CO$ and $CH_4 + CO + H_2$ was found to be 91 and 150 cm. per second respectively, whilst the corresponding calculated values are 78 and 145 cm. per second.

TABLE VI.

Speed of Uniform Movement of Flame in Mixtures of Air with the Mixtures CH_4+CO *and* CH_4+H_2+CO *in a Tube 2·5 cm. in Diameter.*

$CH_4 + CO$.		$CH_4 + H_2 + CO$.	
Combustible gas. Per cent.	Speed, cm. per sec.	Combustible gas. Per cent.	Speed, cm. per sec.
9·45	21·9	7·70	21·2
9·88	36·2	10·01	36·5
12·07	62·5	14·01	83·3
13·73	85·7	15·80	109·4
15·95	91·3	18·92	150·0
18·06	68·9	20·42	148·7
19·32	52·3	22·43	118·5
21·55	19·8	25·05	57·8
		27·57	21·8

FIG. 3.



The speed–percentage curves for the equimolecular mixtures CH_4+H_2, H_2+CO, $CO+CH_4$, and CH_4+H_2+CO are plotted in Fig. 3, the curves for the pure gases being included for comparison.

Mixtures of Industrial Gases with Air.—The equimolecular mixture of carbon monoxide and hydrogen correspond nearly with "water-gas." A coal-gas and a producer-gas were also examined, the compositions of these being:

	Coal-gas. Per cent.	Producer-gas. Per cent.
Benzene and higher olefines	1·1	—
Carbon dioxide	0·3	5·0
Ethylene	2·6	—
Carbon monoxide	9·6	21·3
Hydrogen	49·2	12·6
Methane and higher paraffins	33·9	3·1
Nitrogen (by difference)	3·3	58·0

The speeds of the uniform movement of flame in mixtures of air with each of these two gases are given in table VII.

TABLE VII.

Speed of Uniform Movement of Flame in Mixtures of Air with Coal-gas and with Producer-gas in a Tube 2·5 cm. in Diameter.

Coal-gas. Per cent.	Speed, cm. per sec.	Producer-gas. Per cent.	Speed, cm. per sec.
7·2	21·5	24·7	20·0
10·0	50·5	38·9	47·4
11·9	87·1	46·0	62·7
14·7	133·7	49·0	72·2
16·8	153·9	54·3	69·7
17·9	154·1	58·8	43·5
20·4	115·6	61·6	24·0
21·8	74·3		
24·3	22·0		

The principal constituents of the coal-gas are hydrogen, methane, and carbon monoxide. If all the hydrocarbons be reckoned as methane, the calculated maximum speed of uniform movement of flame in mixtures of air with this coal-gas is 164 cm. per second, with a mixture containing 18·4 per cent. of coal-gas. Since the content of inert gases (nitrogen and carbon dioxide) is low, they may be neglected when making the calculations.

Producer-gas, on the other hand, always contains a large proportion of inert gas; the sample used for these experiments contained only 37 per cent. of combustible gas. For this reason, a value for the maximum speed of uniform movement of flame in a mixture of producer-gas and air, calculated from the maximum speeds in mixtures of the pure gases with air, would be too high.

The speed of flame in mixtures of air with gas containing a large proportion of nitrogen can be calculated on the assumption that the cooling or retarding effect on the flame of excess of air or of nitrogen will be the same, since their specific heats are the same.* A mixture of carbon monoxide, hydrogen, and methane in the pro-

* This assumption is not quite correct, since the presence of reactive gas slightly opposes the retarding effect of air.

portions in which they are found in the sample of producer-gas used in these experiments will have as its "fastest-speed" mixture with air one containing 34·7 per cent. of combustible gases. If nitrogen is added to this mixture, so that the ratio of nitrogen to combustible gases is the same as in the producer-gas, the result is a mixture containing 21·7 per cent. of combustible gases. (The carbon dioxide content being low, it may be calculated as nitrogen.) The speed of flame in this mixture should, on the assumption given above, be but little different from the speed of flame in the same mixture of combustible gases with air. The latter speed is most easily determined by a graphical method, and is found to be 85 cm. per second.

The mixture of air and producer-gas with the fastest speed of uniform movement of flame contains slightly more inflammable gases than is required for complete combustion. A greater "displacement" of the maximum-speed mixture might be expected for the reason that the chief inflammable constituents are hydrogen and carbon monoxide, the individual displacements of which are considerable. The small displacement with producer-gas is due to the presence of inert gases, as will be explained in the succeeding section of this series of researches. The effect, in general, of inert gases on the speed of the uniform movement of flame in gaseous mixtures will also be considered.

ESKMEALS,
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CXXXVIII.—*The Ignition of Ether–Alcohol–Air and Acetone–Air Mixtures in Contact with Heated Surfaces.*

By ALBERT GREVILLE WHITE and TUDOR WILLIAMS PRICE.

OWING to the large number of fires which had occurred during 1917 and 1918 in solvent-recovery stoves in which cordite was being dried, it was decided to investigate the conditions under which mixtures of the vapours of ether, alcohol, and acetone with air would ignite. This was rendered all the more necessary by the fact that the information available on this subject was scanty and often contradictory.

As a general rule, the actual rise in temperature necessary to cause the explosion of such an explosive as glyceryl trinitrate is much lower than that needed to ignite an explosive gaseous mix-

ture. On the other hand, the lower thermal capacity of the gas and its comparatively far greater mobility render it more susceptible to ignition in many cases. There was thus some justification for the idea that the solvent–air mixture was probably responsible for many of the recovery-stove fires that had occurred, particularly when it is remembered that fires had been less frequent in "final" stoves than in recovery-stoves, that more fires had occurred with cordite from which a mixture of ether and alcohol was being removed than when the solvent was acetone, and that ether when mixed with air is indubitably more dangerous than acetone under similar conditions.

The factors affecting the ignition of a combustible gaseous mixture are many, and the influence of some of them is not particularly well understood. The problem of safety when dealing with such a mixture under manufacturing conditions divides itself naturally into two parts, the one dealing with the ignition of the mixture, and the other with the propagation of the flame from one portion of the mixture to another, for example, from one building to another. This division is seen to be inherent when it is remembered that, by using a sufficiently powerful source of ignition, it is possible to ignite almost any combustible gas–air mixture, whereas the propagation of the flame is a totally different matter, particularly if the gas-mixture considered is at rest. In such a case, there appear to be definite limits for the proportion of combustible gas to air in a mixture which propagates flame, these limits depending ultimately only on the direction of propagation and the nature of the combustible gas used, at ordinary temperature and pressure. The experimental work is accordingly divided into three sections:

(1) The ignition-temperatures of various gas-mixtures, including ether–air, alcohol–air, and acetone–air mixtures.

(2) The limits for the propagation of flame in these mixtures.

(3) The investigation of a few miscellaneous facts concerned more particularly with various means of ignition.

The fact has not been lost sight of that ease of ignition and propagation of flame might be enhanced by the presence of some impurity in the solvent vapour–air mixture. Accordingly, experiments have been carried out to ascertain the effect of adding slight amounts of glyceryl trinitrate and of the peroxides of ether to the gas-mixtures dealt with. This was the more necessary, as glyceryl trinitrate, even though present in the stove vapours in minute quantities, is known to be a source of possible danger, and also because there appears to be a tendency to assign any otherwise inexplicable explosion or fire with ether to the influence of these

peroxides (compare Neander, *Chem. Zeit.*, 1902, **26**, 336, and others). This idea seems to have arisen chiefly from the fact that ether which had given trouble had generally been kept for some time, and also because it was well known that the exposure of purified ether to light caused the formation of compounds which appeared to contain active oxygen. The methods used to prepare these compounds were those given by Baeyer and Villiger (*Ber.*, 1900, **33**, 3387; 1901, **34**, 738). Naturally, great care was exercised in freeing the solvents used from such impurities.

The ether used was twice distilled from acid permanganate and washed several times, first with a concentrated solution of potassium hydroxide in water, and then with a dilute one. It was then washed several times with distilled water, dried, distilled, and again dried for several days over sodium. On fractionating twice with a Young and Thomas still-head, a fraction boiling within 0·05° of the boiling point of the pure substance was collected each time. The alcohol used was ordinary absolute alcohol, which was twice heated under reflux for four hours over fresh lime, then twice over calcium turnings for two hours, and refractionated as for ether, the fraction collected boiling within 0·05° of 78·4°. The acetone was purified by converting it into the sodium iodide compound, collecting, and distilling the double compound. The product was then carefully dried and fractionated twice, as in the case of the other compounds. The purity of the solvents used can be gauged from the fact that the acetone obtained had D_4^{20} 0·7808, as low a figure as any published. These solvents were carefully preserved in a dark cupboard.

Except when otherwise specified, percentages can be taken to mean percentage by volume. Tubes are also often specified by their diameters. Thus a tube 5 cm. in diameter would be referred to as a 5 cm. tube.

Section I.

The Ignition-temperatures of Ether–Alcohol–Air and Acetone–Air Mixtures.

With the exception of two figures for ether in air, 1033°, given by McDavid (T., 1917, **111**, 1003) and 190° by Alilaire (*Compt. rend.*, 1919, **168**, 729), the ignition-temperatures found in the literature for the solvents in question are spontaneous ignition-temperatures, which can be taken to be the temperatures at which the substances dealt with (surrounded by oxygen or air at the same temperature) will burst into flame without the application of any spark or other local high temperature. Two sets of these figures, which are intended for engine work, are given. Thus, Holm

(*Zeitsch. angew. Chem.*, 1913, **26**, i, 273) gives the spontaneous ignition-temperature of alcohol in air as 510°, of acetone as 570°, and of ether as 400°. Moore (*J. Soc. Chem. Ind.*, 1917, **36**, 109) gives the spontaneous ignition-temperatures of ether and alcohol in air as 347° and 518°, and in oxygen as 190° and 395° respectively. It will be seen that only the figure given for the ignition-temperature of ether in air by Alilaire, which was published after the completion of our work, appears to be sufficiently low to make an ignition of the solvent–air mixture under present-day conditions of recovery seem feasible.

A paper by Perkin (T., 1882, **41**, 363) on the luminous, incomplete combustion of ether is interesting in this connexion. According to him, this phenomenon was first discovered by Davy, who noticed a pale phosphorescent light round a hot platinum wire. Doebereiner noticed the same thing, and also remarked that when ether was dropped into a retort heated on the sand-bath to 100° and upwards, or into a platinum capsule exposed to the vapour of boiling water, the spheroidal state is produced, accompanied by a blue flame visible only in the dark, and not capable of setting fire to other substances, lachrymatory vapours of lampic acid being formed.

Boutigny and Miller also noted this flame and the products of the combustion, and proved that metal or porcelain dishes were equally effective in producing these phenomena. Boutigny gives the temperature at which ether begins to burn with this flame as a little below that of fusing lead, and so agrees with Perkin and others that the temperature necessary must be about 260°. As will be seen later, however, a temperature much below this is sufficient to produce this flame in ether–air mixtures. According to Perkin, this blue flame has a comparatively low temperature (it has since been designated a "cool" flame). The fingers may be placed in it with impunity. It will neither char paper nor ignite carbon disulphide, and a lucifer match may be held in it for some time before being ignited. He also states, however, that ether vapour burning with this blue flame, when in large quantities, or more especially in a confined space, rapidly increases in temperature and quickly enters into ordinary combustion.

Perkin also examined other substances for "the luminous appearance accompanying incomplete combustion." Only traces of blue flame were obtained with the alcohols up to amyl, methyl alcohol giving none.

The generally accepted definition of ignition-temperature is that temperature to which a gas-mixture must be heated, at least locally, for the speed of the reaction to be such as to become self-support-

ing. This temperature is not that at which a flame appears, but that at which self-heating becomes sufficient to cause ultimate inflammation.

That the determination of an ignition-temperature is a matter of great difficulty can at once be seen when it is considered that the temperature at which such a reaction would become self-supporting must depend on the rate of dissipation of heat in the system as well as on many other factors. For instance, if the time taken to bring the gas-mixture up to the ignition-temperature is appreciable, the composition of the gas-mixture alters, and if a solid is in contact with the heated gases, even below their ignition-temperature, as proved by Bone and Wheeler (*Phil. Trans.*, 1906, [*A*], **206**, 1) and by Meyer and Freyer (*Ber.*, 1892, **25**, 622), the most divergent results are obtained for the amount of combination that takes place. From their work, the German investigators concluded that it was impossible to determine an ignition-temperature.

We decided to try the soap-bubble method described by McDavid (*loc. cit.*), and if that proved unsatisfactory, as was anticipated from Meunier's work (*Compt. rend.*, 1907—1912), to attempt to make use of a method in which the amount of heated surface brought into contact with the gas would be known, thereby eliminating the most obvious defect in the soap-bubble method as published. To this end, it was decided to pass the various gas-mixtures of which the ignition-temperatures were required into certain uniformly heated vessels. In this way, the temperature at which ignition could be obtained in each vessel would be known. By taking vessels of the same material having different ratios of surface to volume and plotting the ignition-temperature against surface per unit volume, it was anticipated that by extrapolation it would be possible to eliminate to a great extent disturbing variations due to surface action. The most obvious vessels to use were tubes of various diameters, and a series of these was accordingly chosen. It was quite realised that the longer time taken to heat a large bulk of gas would affect the results to some extent, but direct experiment, in which some of the products of combustion were introduced into the gas-mixture to be used, soon proved this to be almost negligible in the case of ether–air mixtures of ordinary concentration. It is to be noticed, however, that in this method the temperature determined has been called the sub-ignition-temperature—the minimum temperature at which combination in a gas-mixture becomes self-supporting. This appears to be the practical temperature required, as the phenomenon obtained may or may not give rise to ordinary combustion, depending on circum-

stances. Its identity with the ignition-temperature of a mixture depends entirely on what is understood by "ignition," and a "flame" in those cases in which cool flames are possible phenomena.

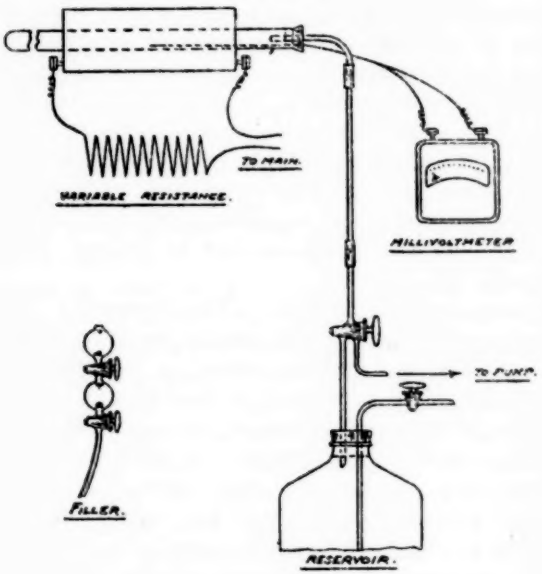
Heating a gas-mixture quickly to its ignition-temperature is always assumed to cause ultimate inflammation. In many cases, an ordinary flame, causing more or less complete combustion, cannot be obtained by heating a gas to its sub-ignition-temperature, and in those cases in which such a flame appears it is only produced through the "cool" flame of incomplete combustion. For a fairly concentrated ether–air mixture, the cool flame obtained is very similar in appearance to an ordinary flame, but for very dilute mixtures it becomes practically a travelling phosphorescent flow.

The Soap-bubble Method.—The results obtained during our investigation of the soap-bubble method of determining ignition-temperatures have already been published (this vol., p. 1248). By using different igniting surfaces, it was found that the ignition-temperature of a 5 per cent. ether–air mixture as determined by this method could vary from 907° to 1064°, whilst that of a 12 per cent. mixture could vary from 870° to 1035°. The results obtained seemed to be erroneous, and by using several gas-mixtures it was shown that the method could scarcely be trusted, even for comparative results.

The Exhausted Tube Method.—The apparatus used in this method is shown in Fig. 1. The heated vessel consisted of a long glass tube sealed at one end and closed at the other by means of a rubber stopper. The tube could be kept at any desired temperature by means of an electric furnace, the exact temperature inside the tube being registered by means of a copper–constantan couple except when that temperature was more than 500°, when a nitrogen-filled mercury thermometer was used. The ignition tube was connected to the glass reservoir containing the mixture under examination by means of a glass lead passing through the rubber stopper. A three-way tap was inserted between the tube and reservoir in such a manner that the tube and lead could be connected at will to the reservoir or to a Gaede box pump. The reservoirs were of 15 to 17 litres capacity, and the tubes used at first were a few cm. longer than the furnace, which was 50 cm. long. The reservoir was filled with any required mixture by exhausting it and allowing air to sweep a known weight of the solvent from the filler, shown in the figure. The filler was connected to the three-way cock by means of rubber tubing, but the end of the filler always projected into the tap tube. In this way, none of the solvent escaped introduction into the reservoir, and a knowledge of the molecular weight of the solvent, together with

the temperature and pressure, gave, by means of a simple calculation, the percentage volume occupied by the solvent in the reservoir. A portion of the lead between the three-way tap and the furnace was connected to the remainder by means of rubber joints. These joints enabled tubes of various internal diameters to be introduced in order to vary the rate at which equalisation of pressure in the tube and reservoir took place. An experiment was conducted as follows. The tube was exhausted to a pressure below 2 cm., and connected to the reservoir by turning the three-way cock as rapidly as possible; an observer, looking through the

FIG. 1.



sealed end of the tube (shielded by a plate of glass), reported whether ignition had or had not taken place.

Shock Ignition.—Preliminary experiments, using 5 to 15 per cent. mixtures of ether in air and a tube 2 cm. in diameter, gave results varying with the diameter of lead used. It was also found that changing the length of the tube from 50 to 100 cm. affected the temperature at which ignition was obtained. These irregularities were presumably due to the differences in time taken to fill the tube with the gas-mixture. Accordingly, a tube 7·5 cm. in diameter was substituted for the one previously used, so that the effect of changing the diameter of the lead could be investigated more easily. With a lead of 1 mm. diameter, ignition took place

at temperatures near 200°, but, on using a lead of 5 mm. in diameter, it was found possible to obtain ignition at from 50° to 60°. These results were obviously too low, and observation showed that they were influenced by the position of the end of the tube relative to the furnace. Experiments were carried out to elucidate this phenomenon, and it was found possible to ignite ether–air mixtures at the ordinary temperature and to ignite other gaseous mixtures at temperatures well below those commonly considered as their ignition-temperatures. The apparatus used consisted of a glass tube 7·5 cm. in diameter, which was connected to a reservoir of 16 litres capacity by means of a glass lead 80 cm. long and of 1·9 cm. internal diameter. By using on the reservoir a cock of 1·5 cm. bore, it was possible to equalise the pressure in the two portions of the apparatus very suddenly. Under these conditions, it was found that when the tube and lead were exhausted and kept at the same temperature as the reservoir (16·5°), ether–air mixtures containing 5 to 15 per cent. of ether were ignited on opening the reservoir cock.

The ignition invariably took place within 15 cm. of that end of the tube remote from the reservoir. In most cases it resulted in a pale blue flame, which travelled quietly along the tube, but sometimes gave inflammation sufficiently violent to shatter the glass. When using 7·5 cm. tubing, ignition could be obtained easily with 60 and 90 cm. lengths, even when the pressure in the reservoir was less than half the atmospheric. Ignition occurred in a 150 cm. tube only when the pressure in the reservoir was greater than three-quarters of an atmosphere. When a 300 cm. tube was used, no ignition could be obtained at the ordinary temperature; a similar negative result was obtained with bottles 30 cm. long and 11·2 to 12·5 cm. in diameter, that is, of approximately the same capacity as the 90 cm. tube. A pad of soft leather in the closed end of a tube of optimum length seemed to prevent ignition at the ordinary temperature, and a plug of cotton wool prevented ignition in precisely the same way. Replacement of the 7·5 cm. tube by one 2 cm. in diameter brought about the same result. It appeared to be immaterial whether highly purified ether or the ordinary commercial variety was used for these experiments. Amongst the other gases tested were mixtures of hydrogen and the vapours of acetone and carbon disulphide with air. Dilute carbon disulphide–air mixtures ignited at the ordinary temperature, acetone–air mixtures below 250°, and hydrogen–air mixtures below 450°, but these experiments were not continued. The information at present available makes it appear highly probable that this ignition is due to the shock caused by the sudden

stoppage of the gas rushing into the exhausted tube. In this connexion, a statement made by Sir Charles Parsons in his inaugural address at the Bournemouth Meeting of the British Association (1919) is of interest. This was to the effect that during the work of a committee appointed by the Admiralty in 1916 to investigate the cause of abnormal propeller erosion, it was discovered that by allowing water to rush into an exhausted conical vessel, a pressure of more than 220 kilos. per sq. mm. was recorded at the apex of the cone. That ignition of a gas-mixture can be produced by a compression wave was demonstrated by Bradshaw (*Proc. Roy. Soc.*, 1907, [*A*], **79**, 236) for mixtures of carbon disulphide in oxygen and for electrolytic gas.

Another factor, the actual rarefaction, must not be forgotten. Investigations by Mitscherlich (*Ber.*, 1893, **26**, 399) on the temperature necessary to explode mixtures of hydrogen and oxygen seem to show that the explosion point is reduced very appreciably by lowering the pressure. Again, Labillardiere, Friedel and Ladenburg, Stock and Guttmann, and others have shown that the temperature necessary for the ignition of mixtures of the hydrogen compounds of phosphorus, silicon, and antimony with oxygen is presumably lowered by reducing the pressure, and that explosion has been known to follow sudden rarefaction. In the course of the work described in this paper, the maximum reduction in sub-ignition-temperature of ether–air mixtures apparently obtained by reduction in pressure alone was only 7°, that is, from 187° to 180°, as shown in Fig. 4. This appears to leave a fair margin for other factors.

The importance of this "shock" ignition is obvious whether it be considered from the theoretical or practical point of view, and it may quite well account for hitherto obscure ignitions met with in the course of solvent-recovery and mine work. The phenomenon underlying shock-ignition must also invalidate a good deal of research work.

Attempt to Eliminate Shock-ignition.—One conceivable method of avoiding shock-ignition in the determination of sub-ignition-temperatures would appear to be that in which the gas is given no appreciable flow before being stopped. An attempt to realise these conditions was made by joining a small bulb on to a gas reservoir in such a way that the distance between the bulb and reservoir was as small as possible. A three-way tap was inserted between the reservoir and bulb to enable the bulb to be exhausted before an experiment. The bulb, which was made of glass, was kept at any desired temperature by being almost entirely immersed in a bath of mercury. When once a connexion had been made

between the bulb and gas reservoir, the tap was turned so as to close both bulb and reservoir. If ignition took place, a flash was easily observed where the bulb-stem emerged from the bath. The bore of the bulb-stem was varied in different determinations. The results obtained when using a 4·5 per cent. mixture of ether in air are given in table I. From them, it will be noticed that the effect of the size of lead is not completely eliminated by this method.

TABLE I.

Showing the Sub-ignition-temperatures of a 4·5 per cent. Ether–Air Mixture obtained by the Bulb Method, using Various Leads.

Diameter of bulb in cm.	Sub-ignition-temperature when lead was		
	Ordinary tube.	Capillary.	Fine capillary.
4·8	178·0°	181·0°	184·0°
4·1	179·0	184·0	185·0
3·5	180·5	185·5	188·0

An interesting point observed in these experiments was the fact that when using a 4·5 per cent. mixture near its apparent ignition-temperature, explosion invariably occurred. On the other hand, when using the bulbs specified above with an ordinary capillary lead and the same gas-mixture, on no occasion did an explosion take place when the temperature of the bath was greater than 197°. Above this temperature, a luminous flash was observed, and nothing more. A 6 per cent. mixture gave similar results, but a 10 per cent. mixture gave no explosion at any temperature tried. An 8 per cent. mixture behaved in precisely the same way as a 10 per cent. mixture, except that on one solitary occasion a violent explosion shattered the bulb. It is possible that a good approximation to the correct sub-ignition-temperature could be obtained by using a very fine capillary tube and a fairly large bulb, but the experiment would not be without danger.

Final Apparatus.—It was found that by making use of a fairly long tube and allowing the sealed end to project well out of the furnace, effects of shock-ignition were apparently eliminated. In this case, the point at which shock-ignition would have occurred in normal circumstances was well outside the heated zone, and on no one occasion was an ignition in the final apparatus observed to start outside the furnace. The lengths of tube used were as follows:

2 cm. tube.	100 cm.
4 cm. tube.	130 cm.
5·5 cm. tube.	130 cm.

The chief difficulty encountered was that of deciding when an ignition had occurred. This was generally easy in the case of

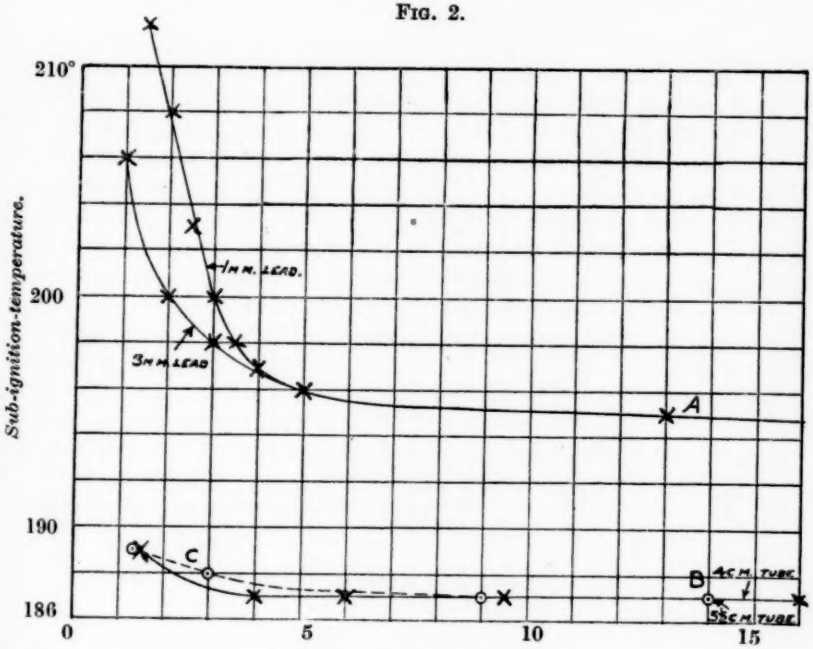
shock-ignition, as not only was the flame fairly easily seen, but the products of combustion had a characteristic and powerful odour. In the case of dilute mixtures of ether in air and ether–alcohol–air mixtures containing small quantities of ether, however, the matter was quite otherwise. It was found almost impossible to distinguish between an ignition and the glow given below the sub-ignition-temperature by combustion on the surface of the glass until travelling was taken as the criterion. This was, of course, due to the fact that the ignition at the lowest possible temperature of a mixture containing ether and air invariably commenced with what has been termed the cool flame. This flame often requires a completely darkened room in order to be visible, but whenever any appreciable quantity of combustible mixture is present, it is liable to develop more or less rapidly into ordinary combustion and, possibly, detonation. That the volume of mixture present is an important factor can be seen from the fact that on no occasion did ordinary combustion develop in the 2 cm. tube within 150° of the sub-ignition-temperature. On the other hand, when using mixtures containing from 5 to 10 per cent. of ether in either of the other tubes, ordinary combustion was liable to develop, and certainly did develop if the temperature was a few degrees above that necessary for inflammation. Test experiments carried out with and without the thermo-couple and thermometer in the tube showed that the presence of these instruments did not appear to affect the result obtained.

Fig. 2 gives the results obtained for the sub-ignition-temperatures of various ether–air mixtures. It will be noticed that in the case of the 2 cm. tube, the results for dilute mixtures differ slightly according to the lead used. This is presumably due to the fact that combustion takes place to a relatively greater extent in the case of the smaller lead, making it more difficult to see the flame at the same temperature. On the other hand, above a certain limit, the internal diameter of the lead does not appear to affect the results obtained with the other tubes. Surface action appears to be negligible in the case of ether–air mixtures of any appreciable concentration if the tube has a diameter of at least 4 cm. That the longer time taken to heat the larger bulk in a wide tube made little difference in the case of ether–air mixtures of concentration greater than about 4 per cent. was proved by adding 1·5 per cent. of the products of combustion of an ether–air mixture to a 5 per cent. mixture of ether in air. The sub-ignition-temperature was only raised 2°. It was found that no difference in sub-ignition-temperature could be detected when purified ether was replaced by the commercial article. It is interesting to note from the shape

of the curve in Fig. 2 that the ignition of ether–air mixtures by this method, depending as it does on the preliminary production of the cool flame, appears to be a molecular process requiring only a certain intensity of molecular movement for its production. The form of curve connecting minimum igniting current with composition of ether–air mixture appears to be quite different.

In Fig. 3 can be seen the sub-ignition-temperatures of certain ether–alcohol–air mixtures as determined in the 2 cm. and 4 cm.

FIG. 2.



Percentage of ether in mixture.

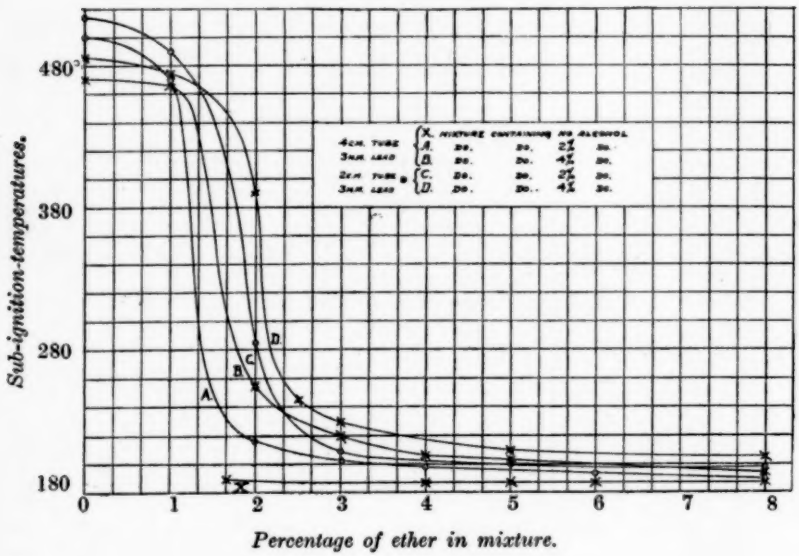
A. 2 *cm. tube,* 1 *and* 3 *mm. leads.*
B. 4 *cm. tube,* 3 *mm. lead.*
C. 5½ *cm. tube,* 3 *mm. lead.*

tubes. The number of points shown on each curve is not great, owing to the fact that the general form of the curves had been previously found when using smaller leads. Each point on the diagram is the mean of three determinations agreeing to within 2° in the case of temperatures below 220° and to within 5° in the case of temperatures above this point.

A consideration of the results given shows that the sub-ignition-temperature of an ether–alcohol–air mixture falls very rapidly when the amount of ether in the mixture is increased from 1 to 2

per cent. This drop is seen to take place with a smaller percentage of ether in the case of the 4 cm. tube, and in both tubes with a smaller percentage of ether in the case of the mixture containing the smaller amount of alcohol. The curves also indicate the manner in which the addition of alcohol to an ether–air mixture affects the sub-ignition-temperature. The elevation in sub-ignition-temperatures is roughly proportional to the amount of alcohol present provided the ether-content lies between 2 and 5 per

FIG. 3.



cent. For comparison, some results, obtained with 4 and 5·5 cm. tubes, are given in table II.

TABLE II.

Showing the Sub-ignition-temperatures of Various Ether–Alcohol–Air Mixtures containing 2 per cent. of Alcohol, as determined in 4 and 5·5 cm. Tubes.

Percentage of ether in mixture.	Sub-ignition-temperature for 5·5 cm. tube. 5 mm. lead.	5·5 cm. tube. 3 mm. lead.	4 cm. tube. 3 mm. lead.
1	495°	500°	470°
2	220	222	217
3	207	210	203
5	201	205	197

The sub-ignition-temperature determined with the 5·5 cm. tube is seen to be higher in every case than that obtained with the 4 cm. tube. This is probably due to the fact that, owing to the larger diameter of this tube, the time of heating is necessarily longer, and hence slow combustion occurs more readily.

With this tube, too, a slight but perceptible difference in sub-ignition-temperature is obtained when using 3 mm. and 5 mm. leads, as shown in table II.

It was seen that in the case of dilute mixtures of ether in air the size of lead used, if small, affected the temperature obtained. This effect was exceedingly marked in the case of ether–alcohol–air mixtures containing little ether. With small leads, it was found impossible to obtain consistent results. For instance, for a mixture of 2 per cent. of alcohol and 1·25 per cent. of ether in air, when using a 1 mm. lead with the 4 cm. tube, a flash would occasionally be obtained below 300°, but one could only be certain of an ignition well above 400°. It was found, however, that if the cock connecting the tube and reservoir was turned on slowly, no ignition was ever obtained below 400°. These differences vanished when leads of 3 mm. or more were used.

The sub-ignition-temperatures of various alcohol–air mixtures are given in table III.

TABLE III.

Showing the Sub-ignition-temperatures of Various Alcohol–Air Mixtures as determined in 2 cm., 4 cm., and 5·5 cm. Tubes.

Percentage of alcohol in mixture.	Sub-ignition-temperature for 2 cm. tube (3 mm. lead).	4 cm. tube (3 mm. lead).	5½ cm. tube (5 mm. lead).
2	515°	500°	520°
3	505	490	505
4	485	470	500
5	480	465	495

In the 4 cm. tube an explosion was often obtained with 4 and 5 per cent. alcohol–air mixtures at 485°. The evidence as to the slower heating of the gaseous mixture in the largest tube is confirmed by the figures given here, as the temperatures found in the case of the largest tube are higher than those for the smallest. It thus appears from the above figures that the nearest possible approach to the correct sub-ignition-temperature of an ether–alcohol–air mixture is obtained by means of a 4 cm. tube. It was found that almost identical results were obtained in the 2 cm. and 4 cm. tubes, whether 2 or 3 mm. leads were used, and that it was not important whether a 3 or 5 mm. lead was used for the

5·5 cm. tube. The sub-ignition-temperatures considered most likely to be correct are summarised in table IV.

TABLE IV.

Showing the Sub-ignition-temperatures of Various Ether–Alcohol–Air Mixtures.

Percentage composition of mixture by volume.			Sub-ignition-temperatures.
Ether.	Alcohol.	Air.	
3—15	0	97—85	187°
8	2	90	189
4	2	94	198
3	2	95	203
2	2	96	217
1	2	97	470
8	4	88	194
4	4	92	206
3	4	93	220
2	4	94	255
1	4	95	465
0	2	98	500 —
0	3	97	490
0	4	96	470
0	5	95	465

The sub-ignition-temperatures of some acetone–air mixtures as determined in tubes of various diameters were found to vary in a manner similar to those of alcohol–air mixtures. The results given below were obtained when using a tube 4 cm. in diameter with a 3 mm. lead.

TABLE V.

Showing the Sub-ignition-Temperatures obtained for some Acetone–Air Mixtures.

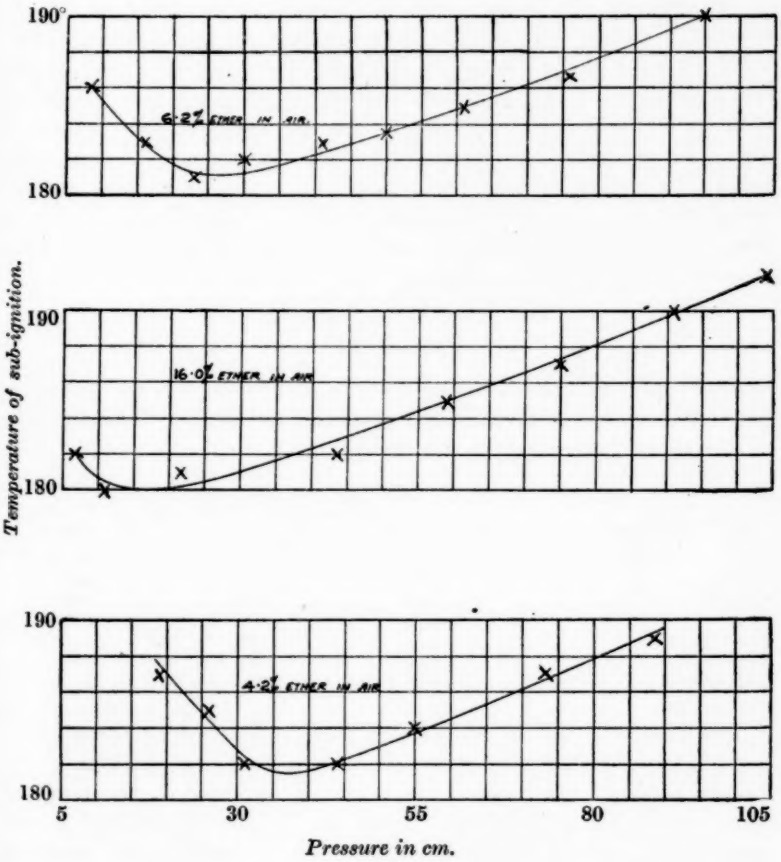
Percentage of acetone in acetone-air mixture.	Sub-ignition-temperature.
4	500°
8	500
Saturated at 15°	505

The ignition found for acetone was very faint at the sub-ignition-temperature, but grew in intensity very rapidly as the temperature of the tube increased.

Influence of Pressure.—During the course of preliminary work on the determination of sub-ignition-temperatures of ether–air mixtures, it was found that consistent results were not obtained for successive experiments when the mixture in the reservoir was not renewed after each determination. This was apparently due to change of pressure inside the reservoir. Several experiments

were therefore made in which the pressure in the reservoir was reduced by pumping out the gas-mixture before firing, and it was found that when the pressure in the reservoir after an experiment was plotted against the sub-ignition-temperature determined, the curves shown in Fig. 4 were obtained. Other mixtures tested in the same way gave precisely similar results, and it was finally found

FIG. 4.



that the easiest method of determining the accurate sub-ignition-temperature of any given mixture under 760 mm. pressure was by starting with a gas-mixture under about 900 mm. pressure and plotting a small portion of the pressure–sub-ignition-temperature curve. The results given in Fig. 2 were obtained in this way. It will be observed that the minimum sub-ignition-temperature

appears to be given at a lower pressure in the case of a mixture rich in ether than in the case of a dilute mixture. This is probably due to the fact that there is a minimum quantity of ether per unit volume necessary to give visible luminosity under any given conditions.

Influence of the Material of the Tube.—A consideration of the results obtained with various tubes shows that it was impossible to eliminate surface action entirely, probably owing to the fact that in the case of the larger tube the heating of a body of gas is necessarily slower. It thus became a matter of importance to discover whether the material of the tube had any influence on the result obtained. The simplest method of effecting this appeared to be by fitting a glass tube with a thin sleeve of the material under test. Accordingly, the 4 cm. tube was fitted with sleeves long enough to project beyond the furnace on either side, these sleeves being made of various metals that might conceivably be used in a manufacturing plant in the presence of gas-mixtures such as those considered. The results obtained are given in table VI.

TABLE VI.

Showing the Results obtained for the Sub-ignition-temperature of Ether–Air and Alcohol–Air Mixtures in a 4 cm. Tube provided with an Internal Metallic Sleeve.

Material of sleeve.	Sub-ignition-temperature.		
	4·3 per cent. of ether in air.	10·5 per cent. of ether in air.	5 per cent. of alcohol in air.
Glass	187°	187°	465°
Copper	175	175	420
Iron	178	178	400
Lead	180	180	—
Zinc	184	184	—
Galvanised iron	184	184	—

The figures given for copper and iron in the case of the alcohol–air mixture can only be regarded as rough approximations, owing to the rapidity with which these metals oxidised at the temperature necessary for ignition. When the metal was oxidised to any appreciable extent, different results were obtained. For instance, the sub-ignition-temperature in the case of a copper sleeve oxidised in the course of ten experiments was 470°. In the case of both ether–air and alcohol–air mixtures, the ignition commenced as a cool flame, but was invariably more violent in the presence of metals, more particularly copper and iron, than with glass.

Influence of the Velocity of the Gas-mixture.—As the gases dealt with in solvent-recovery are generally in motion, it was

decided to investigate to some slight extent the effect of the velocity factor on the sub-ignition-temperatures obtained. Arrangements were therefore made by which the gas-mixture in a reservoir could be displaced by means of water, and the gas from this reservoir made to displace the contents of a second reservoir. The gas-mixture from this second reservoir was passed into a 4 cm. tube 120 cm. long, which was kept at any desired temperature by means of an electric furnace. The far end was partly closed by means of a thick glass plate. It was found that once a steady state had been attained, the velocity of the gas in the tube could be measured sufficiently accurately by estimating the rate at which water was introduced into the first reservoir. An observer looking through the plate glass could easily see if ignition occurred. The sub-ignition-temperature for zero velocity was taken to be the lowest temperature at which ignition occurred after the gas supply had been cut off. The results obtained for two ether–air mixtures are given below in table VII.

TABLE VII.

Showing the Effect of the Velocity of the Gas-mixture flowing through a 4 cm. Tube on the Sub-ignition-temperature observed.

4·5 per cent. of ether in air.		14 per cent. of ether in air.	
Velocity in cm. per second.	Sub-ignition-temperature.	Velocity in cm. per second.	Sub-ignition-temperature.
0	187°	0	186°
6·0	195	1·0	189
12·5	202	5·5	195
—	—	8·0	197
—	—	13·0	202

The experiments carried out were sufficient to indicate that for very small velocities, increase of velocity causes an elevation of the sub-ignition-temperature observed. The velocities dealt with on the manufacturing scale are, however, of a totally different order, ranging from 100 to 400 cm. per second in various pipes.

Influence of the Presence of Glyceryl Trinitrate, Ethyl Hydrogen Peroxide, and Diethyl Peroxide in the Ether Used.—Several attempts were made to find if the presence of glyceryl trinitrate in an ether–air mixture affected the sub-ignition-temperature. In no case was any such effect discernible. In the experiments for which the results are given in table VIII, the glyceryl trinitrate was introduced into the reservoir by passing the air used for making up the mixture through a calcium chloride tube in which glyceryl trinitrate was spread over glass wool, the tube and contents being

kept at 40° to 45°. Results obtained in a 2 cm. tube were similar to those given below, which were determined by using a 4 cm. tube.

Table VIII.

Showing the Effect of the Presence of Glyceryl Trinitrate, Ethyl Hydrogen Peroxide, and Diethyl Peroxide on the Sub-ignition-temperature of Ether–Air Mixtures.

Composition of Mixture.	Sub-ignition-temperature.
5·3 per cent. of ether in air	187°
5·3 per cent. of ether and 1·5 per cent. of diethyl peroxide in air	189
3·7 per cent. of diethyl peroxide in air	189
4·7 per cent. of ether and 0·5 per cent. of ethyl hydrogen peroxide in air	182
5·3 per cent. of ether in air saturated with glyceryl trinitrate at 20°	187

The presence of glyceryl trinitrate did not appear to affect the flame given by the mixture, but the presence of the peroxides caused a very fierce flame and generally an explosion.

It was considered inadvisable to try to determine the sub-ignition-temperature of ethyl hydrogen peroxide in air. The peroxides were found to be exceedingly dangerous to handle; even diethyl peroxide exploded violently on one occasion during distillation.

Section II.

The Limits of Propagation of Flame in Ether–Alcohol–Air and Acetone–Air Mixtures.

Many references are to be found in the literature to the limits of inflammability of mixtures of ether and alcohol with air, and some figures are also given for acetone–air mixtures. The limits determined by various workers are given below.

Ether–Air Mixture.—Limits of inflammability.

2·7 to 7·7 per cent. by volume (Brunswig, "Explosives," first edition, 1912, p. 73).

50 to 60 grams per cubic metre for lower limit (Marchis, *Met. and Chem. Eng.*, 1916, **14**, 190).

2·9 to 7·5 per cent. by volume (Lewes, *J. Soc. Arts*, 1915, 761).

2·9 to 7·5 per cent. by volume (Schwartz, "Fire and Explosion Risks," first edition, p. 35).

0·058 to 0·195 gram per litre (Meunier, *Compt. rend.*, 1907, **144**, 1107).

Alcohol–Air Mixture.—Limits of inflammability.

4·0 to 13·7 per cent. by volume (Brunswig, *loc. cit.*).

4·0 to 13·6 per cent. by volume (Lewes, *loc. cit.*).

3·95 to 13·65 per cent. by volume (Bunte and Eitner, *J. Gasbeleucht*, 1901, **44**, 835).

3 to 8·4 per cent. by volume (Thornton, *Proc. Roy. Soc.*, 1914, [*A*], **90**, 280).

Acetone–Air Mixture.—Limits of inflammability.

5 to 12 per cent. by volume (Brunswig, *loc. cit.*).

2·15 to 9·7 per cent. by volume (Wheeler and Whitaker, T., 1917, **111**, 267).

It will be seen that the results obtained vary considerably, owing to the different conditions under which the experiments were carried out and the various igniting sources used. This is to be expected, as the conditions governing the propagation of flame were not properly appreciated until recent years. The definition now adopted is that suggested by Coward and Brinsley (T., 1914, **105**, 1859), in which inflammability is regarded as a specific property of a mixture, independent of the size and shape of the vessel in which it may happen to be contained, and also of any particular type of igniting arrangement. They propose to define a gaseous mixture as inflammable *per se* at a stated temperature and pressure if, and only if, it will propagate flame indefinitely, the unburnt portion of the mixture being maintained at the original temperature and pressure. On this definition, inflammability is a property of the mixture itself, although a function of the temperature and pressure. Dilution-limits, however, rarely vary much throughout the usual range of variation of laboratory temperature and pressure. It will thus be seen that, in order to obtain satisfactory results in the estimation of dilution-limits, it is necessary to use a vessel (1) of such size that any cooling of the gas-flame by the walls can be neglected, and (2) of sufficient length to enable a sound judgment to be made as to whether a flame would propagate indefinitely or no.

For every gas-mixture examined, propagation-limits were determined for three directions—upward, horizontal, and downward.

Preliminary work seemed to indicate that in a glass tube 5 cm. in diameter, by using a sufficiently powerful initiator, it was possible to force a flame through a mixture below the limit of propagation to the end of the tube, unless it was at least 120 cm. long. All the tubes for limit work were therefore made at least 150 cm. in length.

The tubes consisted of:

(1) Glass tubes 2·5 cm. in diameter.

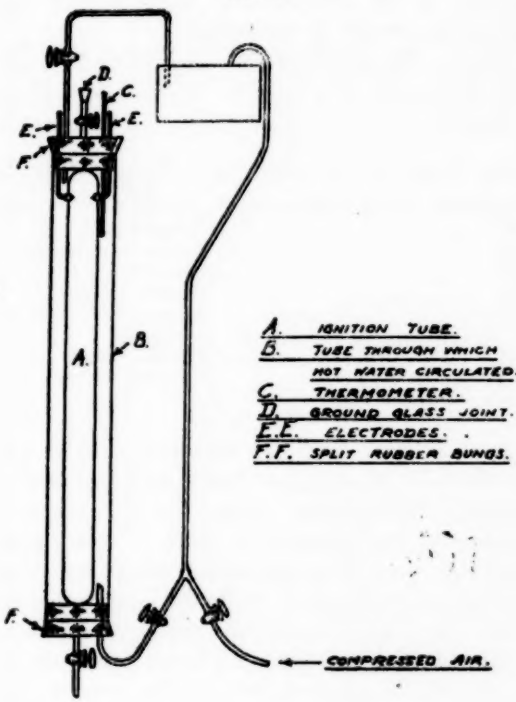
(2) Glass tubes 5 cm. in diameter.
(3) An iron * tube 5 cm. in diameter.
(4) An iron tube 15 cm. in diameter and 300 cm. long.

The glass tubes and the 5 cm. iron tube were 150 cm. long. The glass tubes were closed at both ends by gas-tight stopcocks of 4 mm. bore, and a similar cock was fitted to one end of the iron tube, where a 5 cm. glass observation piece was cemented for observation purposes. The cocks, in the case of the 15 cm. iron tube, were of brass and of 6 mm. bore. In this tube, inflammation was observed through three equidistant windows of thick plate glass, which were cemented into holders on the tube. These windows gave much trouble, and it was found impossible to render them gas-tight by using cement alone. Accordingly, caps were soldered over each window in such a way that, by inserting a 3·7 cm. rubber stopper into the observation hole left in the cap, the whole apparatus could be made gas-tight. The stoppers were removed immediately before firing. This tube was filled by means of a filler similar to that shown in Fig. 1, the end of the filler being made to project well through a tightly fitting piece of rubber tubing drawn over one of the cocks. The filling was carried out precisely as described previously, a correction being always applied for the vapour of the solvent present in the air above the liquid in the filler. In the case of all the smaller tubes, the fillers were provided with ground-glass joints fitting pieces sealed on to the tubes concerned. All the air passed in to make up any mixture containing alcohol or acetone was carefully dried by passage through a calcium chloride tube. The calibration of the tubes was carried out by weighing the quantity of water necessary to fill them. Ignition was effected by passing a spark from an induction coil between two electrodes of stout platinum wire separated by an air gap of 1 cm., the current being obtained from six 2-volt accumulators. In the glass tubes originally used, the platinum was sealed through the glass, but as good sealing glass became scarce, this was found to be impracticable, and the electrodes used for all the tubes consisted of platinum in glass mounted in rubber stoppers. The original method of mixing the gases was by allowing the tube to remain for several hours, but this became inadvisable when rubber was brought into contact with the solvent-laden air. A little mercury enabled efficient mixing to be carried out by shaking the tube, but it was found that this affected the results obtained, and, finally, small glass beads were used. Com-

* This, and the other iron tubes used in the investigation, consisted of terne-plate, that is, sheet-iron coated with an alloy of lead and tin.

parative tests showed that, when using an adequate number of beads, shaking a 5 cm. tube for twenty minutes gave satisfactory mixing. It was also shown that, under these conditions, the same results were obtained whether the electrodes were held by small rubber stoppers or were sealed through the glass. Throughout the course of the work, the only tube that caused trouble was the 5 cm. iron tube. The various cements used for fastening the glass observation cap to the main body of the tube seemed to hold solvent, and the results obtained for this tube cannot be considered

FIG. 5.



as trustworthy as those obtained with the others. The mixing of the contents of the 15 cm. iron tube was done very efficiently by rolling a 12·5 cm. perforated hollow copper ball from end to end.

The apparatus used for determining the upper limit of propagation for alcohol–air and certain ether–alcohol–air mixtures consisted of a 5 cm. glass tube jacketed by enclosure in a wider glass tube, so that hot water could be continuously circulated round it. The arrangement used is shown in Fig. 5.

Two sets of this apparatus were fitted up, one as shown in the

sketch, arranged for experiments on downward propagation, with the electrodes at the same end of the tube as the ground-glass joint for filling the tube, and the other arranged for upward propagation, in which the electrodes were at the end away from the ground-glass joint. For horizontal propagation, either of the above tubes was used and placed horizontally before firing. Some difficulty was encountered in sparking the mixtures contained in this apparatus, but by enclosing the leads in glass tubes, this was finally overcome. Naturally, mixing in these tubes could only be accomplished by allowing the tube to remain for some time.

The procedure in the case of any mixture can be seen by a consideration of the results given below.

Experiment 21.—Glass tube, 5 cm. in diameter.

Solvent mixture used, 75 per cent. of ether and 25 per cent. of alcohol (by weight).

Lower limit, downward propagation. Temperature, 19°.

Percentage of solvent-vapour in gas–air mixture (by volume).	
2·70	Complete ignition.
2·40	Flame just started.
2·60	Complete ignition.
2·50	Partial ignition.
2·55	Flame went nearly to the end.
2·57	Flame went very slowly to the end.

Limit—2·57 per cent.

In the case of a lower limit, an accuracy of 0·02 per cent. was aimed at; in the case of an upper limit, 0·05 per cent. was taken. In every instance, just before firing, the cock furthest removed from the electrodes was opened to allow a free passage for the gases. When the limit of propagation was being determined for a mixture of ether and alcohol, a liquid containing the requisite proportions of these two solvents was made up and used. A test experiment showed that this gave the same result as was obtained when the two solvents were weighed into the tube separately.

Ether–Alcohol–Air Mixtures.—The results obtained for ether–alcohol–air mixtures in glass tubes are shown in table IX.

The experimental results obtained with the 2·5 cm. tubes are not so trustworthy as those determined in larger tubes, as can be seen from the results themselves. For example, the result obtained for the lower limit of an ether–air mixture is least for downward propagation, and other anomalies could be pointed out in the same way. These irregular results were probably due to the fact that it was only for downward propagation that the flame travelled more or less steadily. For upward propagation, it was sometimes

TABLE IX.

Showing the Limits obtained for the Propagation of Flame in Ether–Alcohol–Air Mixtures as determined in Glass Tubes.

The limit figures given show the percentage volume occupied by the total ether–alcohol vapour.

Percentage composition of mixture (by weight).		Diameter of tube in cm.	Direction of propagation.					
			Upwards.		Horizontally.		Downwards.	
Ether.	Alcohol.		Upper limit. Per cent.	Lower limit. Per cent.	Upper limit. Per cent.	Lower limit. Per cent.	Upper limit. Per cent.	Lower limit. Per cent.
100	0	2·5	18·50	2·35	6·15	2·38	6·30	2·34
75	25	,,	6·95	3·15	7·35	3·36	7·35	2·99
50	50	,,	—	3·52	—	3·39	—	3·58
25	75	,,	—	4·35	—	4·45	—	4·40
0	100	,,	—	5·02	—	5·18	—	5·21
100	0	5	15·75	1·93	8·00	2·05	6·15	2·15
75	25	,,	11·70*	2·40	10·95*	2·49	8·35*	2·57
50	50	,,	10·70*	2·89	10·35*	2·99	9·25*	3·05
25	75	,,	12·00*	3·53	11·50*	3·61	10·35*	3·71
0	100	,,	18·95*	4·24	13·80*	4·32	11·50*	4·44

* The figures marked thus were determined in the jacketed tube at 60°, and are, for this reason, not strictly comparable with the others, which were determined at air-temperature (20° ± 2°).

obviously jerked out. Wheeler's work has shown that only a very slight change in the limits takes place when the diameter of the glass tube is increased beyond 5 cm., so that this was the largest size of glass tube used. His work, however, was chiefly carried out with permanent gases.

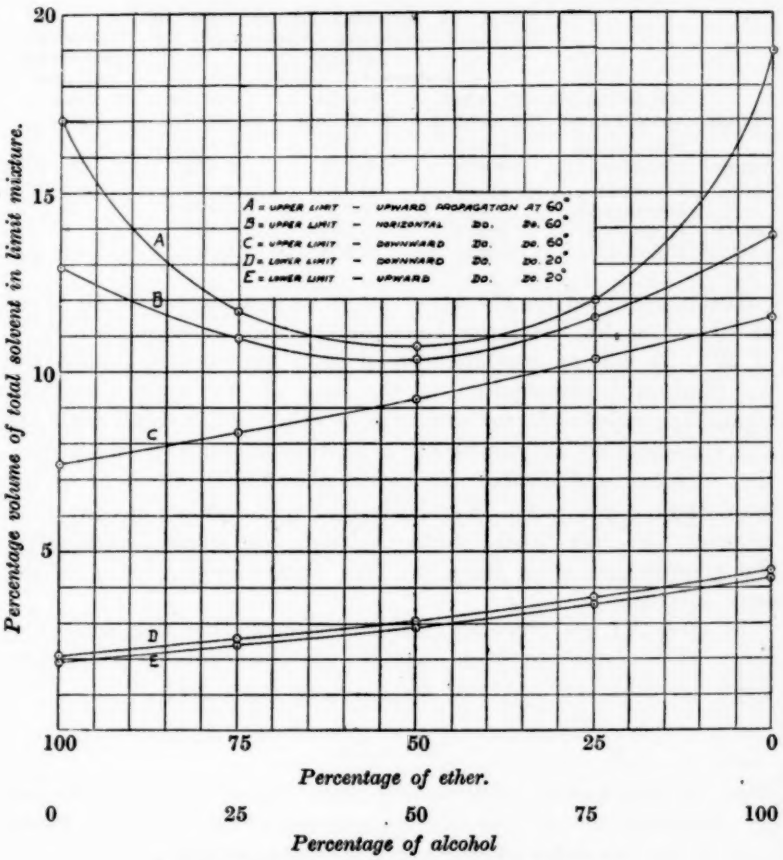
The most noticeable fact brought out in table IX appears to be the great difference between the results obtained for the upper limit for upward propagation and those obtained for propagation in other directions. These differences, which are normally due to convection currents set up by the flame, are not so great for permanent gases. The difference between the upper limits for horizontal and for upward propagation is most marked, and it almost appears as if a different type of propagation were brought into being. It is quite conceivable that the heated gases, rising in the tube, are responsible for the initiation of a cool flame. The difference is not so great in the case of alcohol as it is for ether.

The results for ether–alcohol–air mixtures in a 5 cm. glass tube are shown in Fig. 6. The results given for the upper limits were all determined at 60°. The graphed results for the lower limits and the upper limit for downward propagation form good approximations to straight lines, but this is not the case for the other two curves. At first sight, it seems very strange that, for the upper limit for upward propagation, the results for a mixture containing equal weights of ether and alcohol should be more than 6 per cent. less than the corresponding figure for either ether or alcohol. A possible explanation appears to be afforded by an examination of the sub-ignition-temperature curves given in Fig. 3. From these, it will be seen that the addition of alcohol to an ether mixture raises the sub-ignition-temperature so that the slope of the two upper curves near the 100 per cent. ether point is in the direction to be expected. Similarly, the slope near the 100 per cent. alcohol point can be explained when it is remembered that it takes an appreciable quantity of ether to cause any decided lowering of the sub-ignition-temperature of an ether–alcohol–air mixture. That there is no apparent irregularity corresponding with that seen when the percentage of ether is between 1 and 2 per cent. on the sub-ignition-temperature curves may be due to the fact that so few points have been determined on the limit curve; but it is far more likely to be due to the fact that the sub-ignition-temperature obtained for an ether–alcohol–air mixture containing, say, 2 to 2·5 per cent. of ether, is due solely to the ignition of the ether present, and that the alcohol takes little part in the reaction. These remarks do not apply to curve *C*, Fig. 6,

as in that case the flame obtained is undoubtedly that of ordinary combustion.

The limits of inflammability of a mixture of two or more gases with air are connected with the limits of the components of the mixture by Le Chatelier's rule, which states that if n, n', n'' . . .

FIG. 6.



Composition of solvent mixture used (by weight).

are the percentages of various combustible gases in a limit mixture which will just propagate flame, and N, N', N'' . . . the limiting percentages of the separate gases that can propagate flame, then

$$\frac{n}{N} + \frac{n'}{N'} + \frac{n''}{N''} + \ldots = 1.$$

In table X are given the values for Le Chatelier's constant,

calculated from the results found for various ether–alcohol–air mixtures in 5 cm. glass tubes.

TABLE X.

Showing the Value obtained for Le Chatelier's Constant for Various Ether–Alcohol–Air Mixtures in 5 cm. Glass Tubes at 20±2°.

Limit.	Direction of propagation.	Value of constant in mixture of following percentage composition by weight. 25 ether. 75 alcohol.	50 ether. 50 alcohol.	75 ether. 25 alcohol.	Maximum percentage variation from unity.
Upper	Downwards	0·984	0·971	0·983	3
	Horizontal ...	0·833	0·774	0·830	33
	Upwards ...	0·646	0·589	0·663	41
Lower	Downwards	0·989	0·967	0·980	3
	Horizontal ...	0·995	0·985	0·992	1
	Upwards ...	1·004	0·993	1·007	1

The figures used for the upper limits in this table were all found at 60°, those for the lower being determined, as usual, within 2° of 20°. It will be seen that in all cases for the lower limit and for downward propagation in the case of the upper limit, Le Chatelier's rule holds for mixtures of ether and alcohol with air, and consequently the limits for a mixture containing any proportion of ether and alcohol can be calculated with an error of not more than 3 per cent. For horizontal and upward propagation, however, the rule breaks down entirely. As would be expected, the greatest deviation from the rule always occurs for a 50 per cent. mixture.

In table XI are given the results obtained when the same mixtures were ignited in 5 cm. and 15 cm. iron tubes. The upper limits for ether–air mixtures are given in table XII.

TABLE XI.

Showing the Results obtained in Iron Tubes of 5 and 15 cm. Diameter for the Lower Limits for the Propagation of Flame in Certain Ether–Alcohol–Air Mixtures at 20±3°.

Percentage composition of solvent mixture by weight. Ether.	Alcohol.	Diameter of tube in cm.	Lower limits for propagation of flame. Upwards.	Horizontal.	Downwards.
100	0	5	2·24	2·29	2·34
100	0	15	1·73	1·80	1·93
75	25	15	2·24	2·30	2·46
50	50	15	2·81	2·89	3·02
25	75	15	3·48	3·53	3·69
0	100	15	4·16	4·23	4·37

TABLE XII.

Showing the Upper Limits for Propagation obtained for Ether–Air Mixtures in 5 and 15 cm. Iron Tubes.

Diameter of tube.	Value of limit and direction of propagation.		
	Upwards.	Horizontal.	Downwards.
5	15·45	7·95	6·70
15	23·30	22·30	6·50

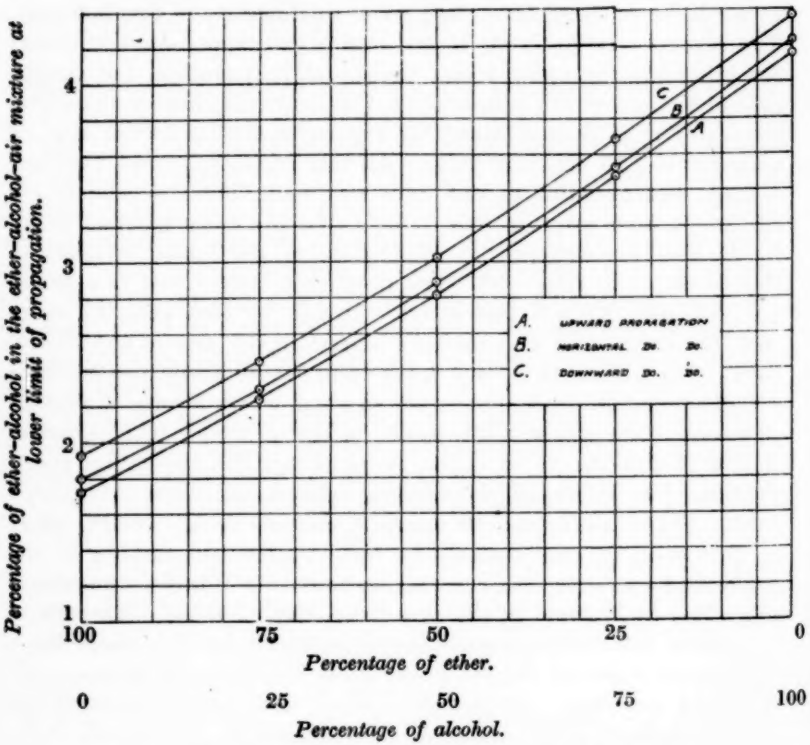
A comparison of these results with those given in table IX shows that for all three directions of propagation, the lower limit, as found for 5 cm. tubes, is greater when the tube is made of iron, as would be expected from the greater conductivity of this material. The reverse relation holds in the case of the upper limit obtained for ether–air for upward and horizontal propagation, but in the case of the downward propagation, the figure obtained for the iron is greater than that obtained for a glass tube of a similar size, or even for the 15 cm. iron tube. As this result appeared peculiar, a fresh determination of this limit was made, but the composition of the limiting mixture was found to be the same as that found in the first experiment. A comparison of the limits obtained in the 15 cm. iron tube with those previously determined (see tables IX, XI, and XII) is instructive. It will be seen that, in every case, the lower limit of a mixture is least in the case of the 15 cm. tube. The difference is very appreciable where a mixture contains a fair amount of ether, but is not so great where alcohol is present in excess. The upper limit, again, is always found to be greatest in the case of the 15 cm. tube, if we except the anomalous result obtained for downward propagation determined in the 5 cm. iron tube. These results may be due to a decrease in the cooling effect of the walls, or may possibly be due to turbulent motion in the gas caused by convection currents, as found by Wheeler and Mason (T., 1917, **111**, 1044) in the case of velocity of flame. An item in favour of the latter supposition is provided by the exceedingly high figure obtained for the upper limit for horizontal propagation in the 15 cm. tube. On the other hand, the flame observed in the case of upward and horizontal propagation in the 15 cm. tube resembled very closely the cool flame of ether, and the characteristic odour following such a flame was observed. The lower-limit results for iron tubes are shown graphically in Fig. 7. The figures in table XIII show that Le Chatelier's rule holds moderately well for the lower-limit results obtained in the 15 cm. iron tube.

TABLE XIII.

Showing the Value Found for Le Chatelier's Constant from the Figures obtained for the Lower Limit for Propagation, using Ether–Alcohol–Air Mixtures in the 15 cm. Iron Tube.

Direction of propagation.	Values of constant given by mixture of percentage composition by weight shown. 25 ether. 75 alcohol.	50 ether. 50 alcohol.	75 ether. 25 alcohol.	Percentage maximum variation from unity.
Downwards	1·028	1·025	1·026	3
Horizontal	1·028	1·036	1·022	4
Upwards	1·039	1·038	1·031	4

FIG. 7.



Composition of the ether–alcohol mixture used (by weight).

Acetone–Ether–Air Mixtures.—Owing to the differences in results obtained for 5 cm. glass and 15 cm. iron tubes, particularly for ether–air mixtures, it was decided to determine the propaga-

tion of flame limits of certain ether–acetone–air mixtures in glass and iron tubes, as it was considered likely that results differing from those published by Wheeler and Whitaker (*loc. cit.*) for acetone–air mixtures would be obtained. The results of our experiments are shown in table XIV, those of Wheeler and Whitaker being given in table XV.

TABLE XIV.

Showing the Propagation of Flame Limits obtained for Acetone–Ether–Air Mixtures, using Various Iron and Glass Tubes at 20 ± 2°.

Percentage composition of mixture by weight.		Material and diameter of tube.	Percentage of solvent in limit mixture and direction of propagation.					
			Upwards.		Horizontal.		Downwards.	
Ether.	Acetone.		Upper limit.	Lower limit.	Upper limit.	Lower limit.	Upper limit.	Lower limit.
0	100	Iron 5 cm.	—	3·80	—	3·90	—	4·00
0	100	Iron 15 cm.	12·40	2·88	12·40	2·89	10·90	3·11
0	100	Glass 5 cm.	12·20	2·89	9·15	3·04	8·35	3·15
25	75	,,	11·20	—	8·55	—	7·75	—
50	50	,,	11·70	2·34	8·25	2·39	7·25	2·49
75	25	,,	13·20	—	8·15	—	6·65	—
100	0	,,	15·75	1·93	8·00	2·05	6·15	2·15

TABLE XV.

Showing the Propagation of Flame Limits as determined by Wheeler and Whitaker for Acetone–Air Mixtures in Glass Tubes of Various Diameters.

Diameter of tube in cm.	Percentage of acetone in limit mixture and direction of propagation.					
	Upwards.		Horizontal.		Downwards.	
	Upper limit.	Lower limit.	Upper limit.	Lower limit.	Upper limit.	Lower limit.
2·5	7·5	2·30	6·7	2·40	6·5	2·75
5·0	9·5	2·20	9·3	2·25	8·3	2·40
10·0	9·7	2·15	9·5	2·20	8·5	2·35

It will be seen that our results differ considerably from those previously published. In most cases, they are considerably higher.

The explanation is almost certainly to be found in the fact that in our method the solvent was weighed directly into the tube, whilst in the other the acetone present in any mixture was estimated by analysis. That our method is the more accurate, as well as the easier, is obvious, but such a large discrepancy can only be explained by some abnormality in the behaviour of acetone during storage if the methods of analysis employed were not faulty. That such abnormal behaviour does take place when acetone vapour is stored over mercury is rendered extremely probable when the facts underlying the molecular association of acetone suggested in the paper by Wheeler and Whitaker are considered.

In this connexion, too, a quotation from the above paper might prove instructive. When discussing the analysis of the mixtures used, the following statement is made: "A supply of air was saturated with acetone vapour at 15° and 760 mm., when it contained 13·5 per cent. (by volume) of acetone, and used as a stock mixture from which the experimental mixtures could be prepared by the addition of air. . . . Consistent results were obtained by either of the absorption methods of analysis. Thus, a mixture, *known to contain about* 6·5 *per cent.* of acetone, gave on analysis:

"(1) Sodium hydrogen sulphite method . . . 6·50, 6·45, 6·54, 6·55.

"(2) Distilled water . . . 6·40, 6·56, 6·54, 6·50, 6·51, 6·51.

"Absorption by distilled water seemed, therefore, to afford a sufficiently accurate method of analysis."

The mixture "known to contain about 6·5 per cent. of acetone" was apparently made up by diluting the requisite quantity of the stock solution with a calculated volume of air. The accuracy of the method of analysis appears to be assumed from the fact that results approximating closely to the calculated figure were obtained. An examination of published figures for the vapour pressure of acetone at 15°, however, shows that a stock solution of air saturated with acetone vapour at this temperature at 760 mm. pressure would contain more than 19 per cent. of acetone (by volume), the vapour pressure of acetone at 15° being given by Sameshima (*J. Amer. Chem. Soc.*, 1918, **40**, 1482) as 147 mm. Extrapolation from Regnault's results gives a very similar figure—about 150 mm. Raising Wheeler and Whitaker's results in the ratio of 19:13·5 would often bring them much nearer to those obtained by us.

The results obtained for lower limits in the 15 cm. iron tube are strikingly similar to those obtained in a 5 cm. glass tube (see table XIV), and for upward propagation the upper limits are also very near. There are, however, very marked differences in the other figures given for the upper limits. It is worthy of note that

the upper limits for upward and horizontal propagation are here identical in the case of the 15 cm. tube. The results obtained when using the 5 cm. iron tube show clearly what a large effect the conductivity of the material of the tube has in this case. The results obtained in 5 cm. glass tubes for the propagation of flame limits of ether–acetone–air mixtures are shown graphically in

FIG. 8.

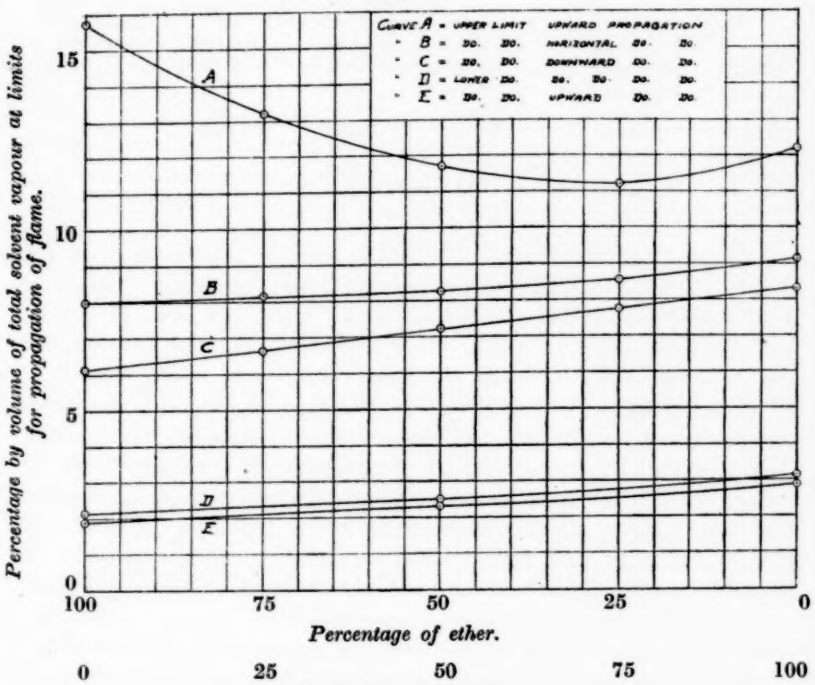


Fig. 8. It will be noticed that the upper-limit curves present the peculiarities commented on in the case of ether–alcohol–air mixtures, although to a less extent.

The figures given in table XVI show that Le Chatelier's rule holds moderately well for ether–acetone–air mixtures, except in the case of the upper limit for upward propagation.

TABLE XVI.

Showing Values obtained for Le Chatelier's Constant for the Limits for Propagation, using Ether–Acetone–Air Mixtures in the 5 cm. Glass Tube at 20±2°.

Limit.	Direction of propagation.	Value of constant given by mixture of percentage composition by weight shown. 25 ether. 75 acetone.	50 ether. 50 acetone.	75 ether. 25 acetone.	Percentage maximum variation from unity.
Upper	Downwards	0·997	1·005	0·997	1
Upper	Horizontal	0·962	0·959	0·981	4
Upper	Upwards	0·875	0·866	0·910	13
Lower	Downwards	—	0·952	—	5
Lower	Horizontal	—	0·953	—	5
Lower	Upwards	—	0·987	—	1

Influence of Temperature.—The influence of temperature on the limits of inflammability of gaseous mixtures has been studied by Bunte and Roszkosski (*J. Gasbeleucht.*, 1890, **33**, 491, 524, 535, 553), Taffanel (*Compt. rend.*, 1913, **157**, 595), Burrell and Robertson (*United States Bureau of Mines, Technical Paper* No. 121, 1916), and Mason and Wheeler (T., 1918, **113**, 45). The experimental work of Bunte and Roszkosski appears to have been defective, but the other workers found that the inferior limit of inflammability of methane–air mixtures was lowered by increasing the temperature of the gas-mixture before ignition. Mason and Wheeler also showed that the upper limit of inflammability of methane–air mixtures became much greater under these conditions, so that increasing the original temperature of the gas widens the limits of inflammability of methane–air mixtures. This would be expected from the fact that the self-propagation of a flame through a combustible mixture is only possible when the heat due to the reaction between the combining gases is sufficient to make up for losses due to radiation, conduction, and convection, whether the heat lost is dissipated or utilised in raising adjacent layers of the gas to the inflammation temperature. The heat of reaction necessary and the heat dissipated must obviously be less in the case where the original temperature of the gaseous mixture is higher. A few figures are given below to show to what extent the limits of inflammability are affected by temperature.

TABLE XVII.

Showing some Results obtained by Mason and Wheeler for the Downward Propagation of Flame in Mixtures of Methane and Air.

Initial temperature.	Lower limit.	Upper limit.
20°	6·00	13·40
100	5·45	13·50
200	5·05	13·85
300	4·40	14·25
500	3·65	15·35
700	3·25	18·75

In the circumstances, it was decided that it would be unnecessary to do more than find the change in the upper limit of ether–air mixtures with temperature. These experiments were carried out in the jacketed tube utilised for the upper limits of alcohol and ether–alcohol–air mixtures. The results obtained are shown in table XVIII. It will be seen that a decided rise in the upper limit for propagation takes place when the initial temperature of the mixture is raised through 40°.

TABLE XVIII.

Showing how the Upper Limit for the Propagation of Flame Varies with the Initial Temperature of the Ether–Air Mixture Used.

Direction of propagation.	Limit at 20°.	Limit at 60°.
Upwards	15·75	17·05
Horizontal ...	8·00	13·00
Downwards ...	6·15	7·45

Influence of Pressure.—The influence of pressure on the limits of inflammability of gases over any large range is by no means easy to predict, although it is well known that the lower limit of inflammability of many gas–air mixtures increases at diminished pressures. Terres and Plentz (*J. Gasbeleucht.*, 1914, **57**, 990, 1001, 1016, 1025), Burrell and Robertson (*loc. cit.*), and Mason and Wheeler (*loc. cit.*) have investigated the effect of pressure on the limits of inflammability of mixtures of methane with air. The general conclusions to be drawn from their work appear to be that, below atmospheric pressures, decreasing the pressure narrows the limits of inflammability, but that above atmospheric pressure, increasing the pressure raises both the limits of inflammability.

The work done by us was confined to pressures at or below atmospheric pressure, and the results are shown in table XIX and XX.

TABLE XIX.

Showing the Influence of Pressure on the Limits for Horizontal Propagation of Flame in Ether–Air Mixtures.

Pressure in mm.	Percentage of ether in mixture. At lower limit.	At upper limit.
770	1·87	—
751	—	12·90
600	—	10·50
520	—	9·20
460	1·88	—
450	—	8·20
420	—	7·90
400	—	7·80
300	1·92	7·30
200	2·08	6·80
100	2·33	6·10
50	2·99	5·00

TABLE XX.

Showing the Influence of Pressure on the Limits for Downward Propagation of Flame in Ether–Air Mixtures.

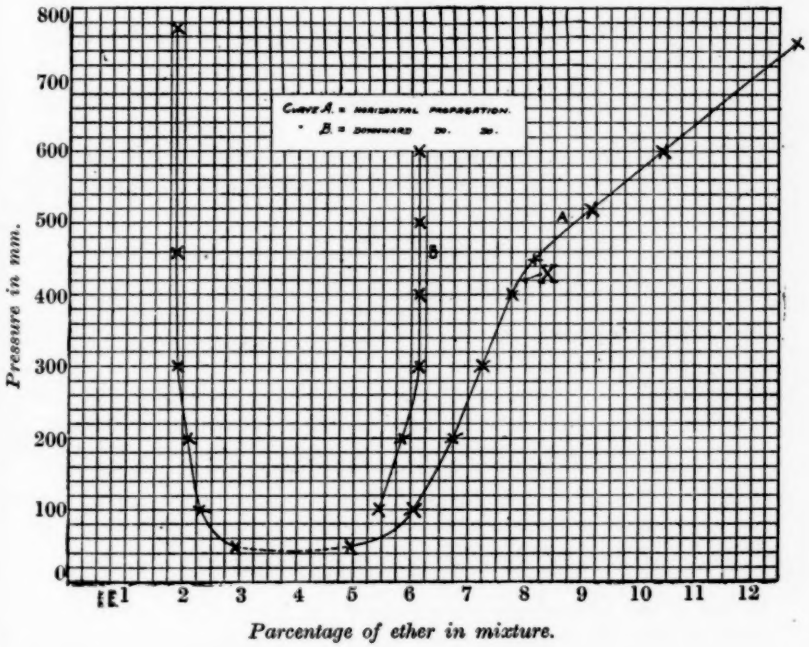
Pressure in mm.	Percentage of ether in mixture at lower limit.
600	6·20
500	6·20
400	6·20
300	6·20
200	5·90
100	5·50
50	No ignition.

It will be noticed that the results obtained near atmospheric pressure in the case of these experiments differ appreciably from those found by the ordinary method as given in table IX. This is due to the fact that all the experiments given in tables XIX and XX were carried out with both cocks closed. The type of ignition obtained was also very different; for instance, the ignitions obtained when determining the upper limit for horizontal propagation under 600 and 751 mm. pressure were characteristic, slow, cool flames which could not be seen except in a totally darkened room. It was found that any attempt to determine the limits for propagation of ether–air mixtures for pressures greater than atmospheric in the glass tubes available merely shattered the tube. The curves given by plotting pressure against the percentage of ether in the limiting mixture are given in Fig. 9. That for horizontal propagation is interesting. It was at pressures above that at the peculiar bend marked × that the cool flame became notice-

able. Below this pressure the flame was of a green colour and traversed the tube very rapidly in a manner similar to that noticed for the lower limit at corresponding pressures.

Influence of Velocity.—Under present-day conditions of solvent-recovery, a good portion of the solvent–air mixture is often in rapid motion. It therefore became a question of determining, so far as was possible in the laboratory, the effect of velocity on the limits of propagation of solvent–air mixtures. Owing to the fact that no

FIG. 9.



real approximation to manufacturing conditions could be attained, the work done was confined to ether–air mixtures.

It has long been known that a moving mixture of combustible gas and air, too weak to propagate flame, can carry a cap of flame to a great distance from an igniting source. Wheeler has also proved that a mixture below the lower limit of propagation, when in a quiescent state, can often inflame when agitated. The speed of propagation of flame is also notably dependent on the degree of mechanical agitation of a mixture, and various experiments on the effect of agitation on gas-mixtures and on the rate of development of pressure when gas-mixtures are ignited are given by Clerk and

Hopkinson (*Rep. Brit. Assoc.*, 1912, 200), Clerk ("Ganet Lecture," Junior Institution of Engineers, 1913), and Wheeler (this vol., p. 81). So far as we know, however, no figures have as yet been given for the effect of the velocity of a gas-mixture on the limits of its propagation of flame.

The methods used for moving the mixture and determining its velocity were those described under sub-ignition-temperature. Great care had to be taken in determining the upper limit for propagation against the gas-current, as the flame passed with great velocity down the 10 mm. bent glass tube joining the limit tube to the reservoir. This gave very little time for preventing the flame from getting into the reservoir. The results obtained are given in table XXI.

TABLE XXI.

Showing the Effect of the Linear Velocity of an Ether–Air Mixture on its Downward Propagation of Flame Limits, as determined in a 5 cm. Glass Tube at 20±2°.

Velocity in cm. per sec.	Percentage of ether in mixture at lower limit.	Percentage of ether in mixture at upper limit.
Flame moving in the direction of gas current.		
0	2·13	6·15
1	1·97	6·40
3·5	1·95	6·50
9	1·95	6·65
Flame moving against the gas current.		
0	2·13	6·15
1	—	6·25
3·5	—	6·25
9	—	6·25

It was found to be impossible to find the lower limit of propagation when the flame was moving against the stream, as it merely became a question of the velocity of the stream as compared with that of the flame in the mixture used. It will be seen from the upper portion of the table that the velocity of the gas-current affects very appreciably the percentage mixture which will propagate flame. That a portion of this change is due to turbulence caused in the gas, however, appears to be very likely, for, in the cases tried, when the flame moves against the gas-current with any real velocity, the upper limit is always the same.

The figures given for zero velocity in table XXI are those found with one cock closed in the ordinary manner. As conditions are slightly different when both cocks are open, it was decided to try such an experiment. The upper limit found under these conditions

was 6·30 per cent., but the convection due to the flame probably caused this figure to be a little high, on account of the air drawn into the tube during the passage of the flame. It almost appears as if, when a flame is travelling against a gas-stream, the turbulence due to the velocity of the stream practically balances the effect of that velocity in hindering the propagation of flame.

Influence of the Presence of Glyceryl Trinitrate, Diethyl Peroxide, and Ethyl Hydrogen Peroxide.

In the experiments to determine the effect of glyceryl trinitrate on the limits of propagation for ether–air mixtures, the mixture used was charged with glyceryl trinitrate, as described under the experiments on the determination of sub-ignition-temperatures. The results obtained when using ether–air mixtures containing diethyl peroxide and ethyl hydrogen peroxide are given in table XXII.

TABLE XXII.

Showing the Effects on the Limits of Propagation of Flame of adding Amounts of Glyceryl Trinitrate, Diethyl Peroxide, and Ethyl Hydrogen Peroxide to Certain Ether–Air Mixtures.

Direction of propagation.	Limit.	Mixture used (with air).	Percentage of ether in limit mixture.
Upwards	Lower	Ether.	1·93
Downwards ...	"	"	2·15
"	Upper	"	6·15
Upwards	Lower	Ether saturated with glyceryl trinitrate at 20°.	1·95
Downwards ...	Upper	"	6·15
"	Lower	Diethyl peroxide.	2·34
"	"	Ether containing 25 per cent. of diethyl peroxide by weight.	2·18
"	Upper	"	10·1
"	Lower	Ether containing 10 per cent. of 80 per cent. ethyl hydrogen peroxide by weight.	2·17
"	Upper	"	6·5

The peroxides of ether are calculated as ether in making up the percentage volume occupied by the solvent in the limiting mixture. It will be seen that glyceryl trinitrate appears to have no effect on either limit, and that the peroxides have little effect on the lower limit, but that they raise the upper limit very appreciably.

The glyceryl trinitrate did not appear to affect the flames given, but the flames, when peroxides were present, were invariably fiercer than when ether alone was used, except, perhaps, at the extreme limit.

Section III.

Investigation of Various Means of Ignition.

A series of experiments was carried out in which sparks obtained by various means were used for attempting to ignite ether–alcohol–air mixtures. It was found that steel to steel, emery to steel, and pyrites to steel sparks appeared to be unable to cause the inflammation of any of the many mixtures tested. Ferro-cerium to steel sparks, however, ignited most mixtures very readily. The igniting powers of a small gas flame and a moderately powerful electric spark appeared to be of the same order, and both almost invariably gave rise to ordinary combustion, the limits of propagation of flame being naturally identical in the two cases. In the case of ether–alcohol–air mixtures, quick heating of a mixture, up to, but not far above, its sub-ignition-temperature, seemed to give rise to a cool flame which had limits for propagation varying from those of ordinary inflammation.

The Cool Flame.—The difference in propagation-limits for the two methods of combustion was particularly noticeable in the case of concentrated ether–air mixtures, as the flame travelled easily through a 20 per cent. mixture in a horizontal tube 4 cm. in diameter, although the upper limit for the propagation of ordinary combustion in a 5 cm. tube would be 8 per cent. No determinations of the limits for propagation of a cool flame were made, but experiments carried out for other purposes indicate that it is unlikely that such a flame could propagate downward through a mixture containing much more than 6 per cent. of ether. This flame was occasionally observed when electrical ignition was utilised, more particularly with high concentrations of ether or low pressures. It appeared, as stated by Perkin, to require very little oxygen, and the products of combustion were characteristic. It was found that the addition of less than 1 per cent. of oxygen to a mixture of 9 per cent. of ether in nitrogen was sufficient to give luminous combination below 220°. The increase of temperature caused by this flame in a mixture containing less than 3·5 per cent. of ether and heated to its sub-ignition-temperature was insufficient to be indicated by the fine thermo-couple registering the temperature of the gas in the ignition tube. The increase of pressure caused by it was also very small. This was measured roughly by its effect on a column of mercury so arranged that after ignition the mercury in both limbs of a U-tube would be level. The mean of three experiments with a 3·9 per cent. mixture gave a momentary

increase of pressure equal to 3 or 4 cm. Mixtures containing more ether gave far greater pressures.

It was found that a 0·3 cm. mesh iron gauze, or a 0·2 cm. mesh brass gauze, prevented the passage of a cool flame down a glass tube 7 cm. in diameter.

Discussion of Results.

The sub-ignition-temperature figures given above agree fairly well with ignition-temperatures previously published for alcohol and acetone. The sub-ignition-temperature given for ether–air mixtures, however, whilst agreeing almost exactly with the ignition-temperature given by Alilaire, differs notably from the other figures available. The difference is probably to be accounted for by the fact that in the methods employed to obtain these, no account was taken of the cool flame of ether—the cool flame of alcohol can only be obtained near the temperature at which an explosion or ordinary combustion occurs directly. This may be justifiable and necessary in the determination of ignition-temperatures, but involves the neglect of a phenomenon which can, and very often does, give rise to ordinary combustion under suitable conditions. Moreover, these conditions are precisely those liable to obtain during solvent-recovery on the manufacturing scale, namely, the presence of a large volume of the solvent–air mixture and some degree of confinement.

That ordinary combustion of a dangerous nature could be caused by heating an ether–air mixture in glass tubes to 187° was proved again and again when using 4 and 5·5 cm. tubes, particularly if the percentage of solvent lay between 5 and 9. That this result was a genuine one was proved by stopping a current of ether in air flowing along a glass tube kept at 187°. Ignition of the ether occurred in every case. The method employed to determine sub-ignition-temperatures thus appears to be a practical one, and also has the advantage of being easily adaptable to determine the effect of substituting for glass any material that might be used in manufacture.

The ignition observed by Alilaire must indubitably have commenced as a cool flame. The temperatures necessary to obtain such a flame in mixtures containing fair quantities of ether, as shown by us, are fairly near the temperatures attainable in a steam-heated building, particularly when it is considered that the presence of metals lowers the sub-ignition-temperature appreciably. On the other hand, the results previously obtained for the ignition-

temperature of ether–air mixtures are far above those one can conceive of being attained in such a building, except in the most extraordinary circumstances.

The results show that a quiescent gas appears to be more easily ignited than one in motion, but the experimental work covers only a very small range of velocities, and in any case the propagation of flame is more easily and quickly carried out by gas in motion.

The presence of glyceryl trinitrate in a gas-mixture, as was anticipated from its amount, does not seem to affect the temperature of sub-ignition or the limits of propagation of flame. The peroxides sometimes present in ether in very small amounts can, however, affect both its ignition and its propagating qualities if present in sufficient quantity. Our work seems to indicate that their influence in causing primary ignition could only be inappreciable, although it is quite conceivable that they could well affect the change from cool to ordinary flame.

Reduction of pressure appeared to cause a lowering of the sub-ignition-temperature of the mixtures examined, but the effect of pressure alone within the range of variation of atmospheric pressure can scarcely have a practical influence on the ignition of the solvent–air mixtures, as for ether–air, for example, a reduction of pressure of 10 cm. near atmospheric pressure caused a variation in the sub-ignition-temperature of less than 2°.

The only phenomenon that could be expected to reduce the sub-ignition-temperature of ether–alcohol–air and ether–air mixtures below the danger limit is thus that described as shock ignition. With a difference of pressure of less than half an atmosphere, it was possible by this method to ignite a gas-mixture at least 170° below its sub-ignition-temperature, so that it is quite conceivable that the development of sudden differences of pressure on the manufacturing scale might easily be the determining factor in bringing about ignition of the solvent-laden air. Exactly how this is to be brought about can only be conjectured, as our inside knowledge of gas-ignition, particularly as regards this fresh phenomenon, is very limited. The present work has shown how many accidents could happen, but much remains to be done before any sound explanation can be given of such a conflagration as was described in *The Times* of March 28th, 1919, when a bottle of ether exploded in a military hospital at Southage. According to the same report, explosions of bottles of ether are of somewhat frequent occurrence.

The results given in the older work for the limits for propagation of flame in ether–air mixtures are 1·8 per cent. and about 9 per cent., the latter being apparently far out, whilst those for alcohol–air mixtures agree fairly well with our results, particularly

as regards the lower limit. The change from 5 cm. glass to 15 cm. iron tube affects the results for the upper limit for horizontal and upward propagation in ether–air mixtures very materially, the limits becoming well over 20 per cent. in each case, instead of 8 per cent. for horizontal propagation and 16 per cent. for upward propagation. The extreme limits determined for ether–air mixtures are thus 1·73 and 23·30 per cent. The upper limit for propagation in alcohol–air mixtures in 5 cm. glass tubes was found to be 18·95 at 60°. As this figure was well above the highest concentration of alcohol vapour obtainable during normal recovery, there was no point in repeating this in the 15 cm. iron tube. The lower limit of propagation for alcohol–air mixtures was only very slightly altered in the large iron tube, falling from 4·24 per cent. in the 5 cm. glass tube to 4·16 per cent.

The results for the propagation of flame in ether–alcohol–air mixtures obtained during this investigation are distinctly interesting. It is found that Le Chatelier's rule holds for all directions of propagation for the lower limit, and for the upper limit for downward propagation. The rule does not hold for the other two directions of propagation for the upper limit, the discrepancies being very considerable in the case of upward propagation. Wheeler's work on acetone–air mixtures has already been discussed, and it may suffice here to state that the limits given by him are 2·15 and 9·7 per cent., our results being 2·88 and 12·40 per cent. The lower limit of 5 per cent. given by Brunswig is obviously wrong, but the upper-limit figure of 12 per cent. is very near that found by us.

It will be seen that the effect of temperature and pressure on the limits for the propagation of flame in ether–air mixtures is quite material. The influence of the velocity of the gas-current was not examined throughout a sufficient range to enable sound conclusions to be drawn as to its effect under manufacturing conditions, but it is fairly clear that a margin must be allowed for this factor when dealing with the limit results obtained. The presence of 1 per cent. of the peroxides of ether in ether–air mixtures appears to have no appreciable effect on the lower limit for the propagation of flame, and it is by no means likely that there would be sufficient peroxide present under practical conditions to affect the upper limit materially.

Summary.

The soap-bubble method described by McDavid (*loc. cit.*) gave for the ignition-temperature of ether–air mixtures results varying from 859° to 1068°. The method seemed to be untrustworthy.

The other method used seemed to give the minimum temperature at which the reaction in a combustible gas-mixture became self-supporting—called the sub-ignition-temperature. This temperature, which appears to be the one required from a safety point of view, was 187° for ether–air mixtures in glass, and varied from 187° to about 500° for the different ether–alcohol–air mixtures used. It was about 500° for acetone–air mixtures. The presence of appreciable quantities of metal in the vessels used lowered the sub-ignition-temperature.

Decrease of pressure appeared to reduce the sub-ignition-temperature of a mixture, but the presence of small quantities of glyceryl trinitrate or of diethyl peroxide had little effect on the sub-ignition-temperature of ether–air mixtures. The sub-ignition-temperature of such mixtures was lowered by the presence of ethyl hydrogen peroxide. The effect of slight velocities seemed to be to raise the sub-ignition-temperature of ether–air mixtures.

When an exhausted vessel is quickly put into communication with a reservoir containing ether–air or carbon disulphide–air mixtures, under specified conditions the gas can be ignited at the ordinary temperature. This phenomenon has been termed shock ignition.

The limits for the propagation of flame in mixtures of ether–alcohol–air and ether–acetone–air have been determined in 2·5 and 5 cm. tubes of glass and in 5 and 15 cm. tubes of iron. The extreme limits found were 1·73 and 23·30 per cent. for ether–air mixtures, 4·16 and 18·95 per cent. for alcohol–air mixtures, and 2·88 and 12·40 per cent. for acetone–air mixtures. The upper limit for propagation in alcohol–air was determined at 60°. Figures obtained with the 15 cm. iron tube often differed appreciably from those obtained with 5 cm. glass tubes.

Le Chatelier's rule was found to hold fairly well for ether–alcohol–air mixtures, except for horizontal and upward propagation in the case of the upper limit. The only considerable deviation from the rule in the case of ether–acetone–air mixtures was observed for upward propagation and the upper limit.

Increase of temperature was found to raise the upper limit for propagation in ether–air notably, and reduction of pressure was found to narrow the limits. Increase in the velocity of the gas-mixture widened the limits materially. The presence of the peroxides of ether scarcely affected the lower limit of propagation in ether–air, but any considerable quantity raised the upper limit of such a mixture.

It was found impossible to ignite ether–alcohol–air mixtures by means of steel to steel, emery to steel, or pyrites to steel sparks, but

inflammation was readily obtained when using ferro-cerium to steel sparks.

Many of the properties of ether–air mixtures appear to be explained by the formation of a cool flame.

Further work is contemplated on the phenomenon referred to as shock ignition.

We desire to express our thanks to Messrs. Nobel's Explosives Co., Ltd., for whom the work was carried out, and particularly to Mr. W. Rintoul, Manager of the Research Section, for kind permission to publish our results. We also wish to thank Mr. A. W. Sanderson for assistance in carrying out some of the experimental work.

THE RESEARCH LABORATORIES,
ARDEER FACTORY, STEVENSTON. [*Received, September 22nd,* 1919.]

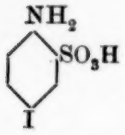
CXXXIX.—*The Conductivities of Iodoanilinesulphonic Acids.*

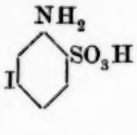
By MARY BOYLE.

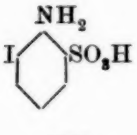
No systematic study of the halogen-substituted derivatives of the anilinesulphonic acids seems to have been attempted. Eight out of the ten possible monochloro-, about five of the monobromo-, and three monoiodo-derivatives have been described by P. Fischer, Post, Meyer, Bahlmann, etc., but in some cases the constitution is left uncertain and in most others there is merely a simple statement of the preparation and properties of individuals; owing to the incomplete character of the group, no comparative study of either the chloro-, bromo-, and iodo-substituted derivatives or of the different members of a group of acids substituted by one particular halogen has been possible. It was thought that it might be interesting to study one particular property throughout a complete series, in order to determine how the value of that property is affected by the position in the nucleus taken by the halogen relative to the two other groups present. The series chosen was that of the iodoanilinesulphonic acids, and the property that of electrical conductivity.

So far, however, it has not been found possible to prepare the

ten possible isomerides, but the following eight, of established constitution, are now known:


(I.)


(II.)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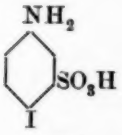
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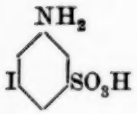
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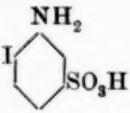
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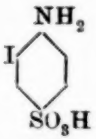
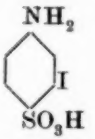

(VII.)


(VIII.)

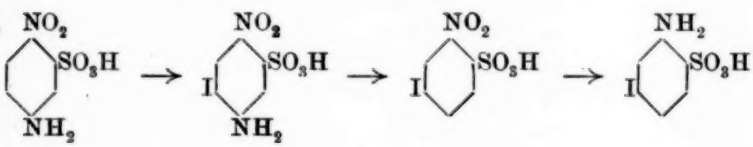
The series of chloroanilinesulphonic acids described by P. Fischer, Meyer, Claus, Goslich, Limpricht, etc., corresponds closely with the above, except that the chloro-analogue of III is unknown, and that a 3-chloroaniline-2-sulphonic acid described by Post and Meyer has no counterpart, up to the present, among the iodine compounds.

2-Iodoaniline-4-sulphonic acid (VII) was described in a patent by Kalle & Co. (D.R.-P. 129808), and its constitution established in 1909.

4-Iodoaniline-2-sulphonic acid (I) and 3-iodoaniline-4-sulphonic acid (VIII) were described by the author in 1909 (T., **95**, 1689, 1709).

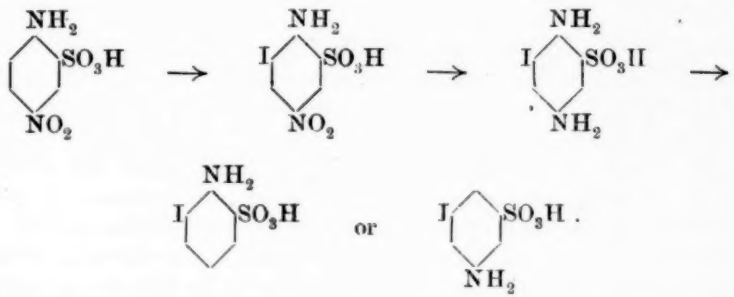
The others have been prepared from various nitroanilinesulphonic acids, as described below.

5-*Iodoaniline-2-sulphonic acid* (II) was obtained from *p*-nitroaniline-*m*-sulphonic acid by treating it with iodine chloride, removing the amino-group, and subsequently reducing the nitro-group.



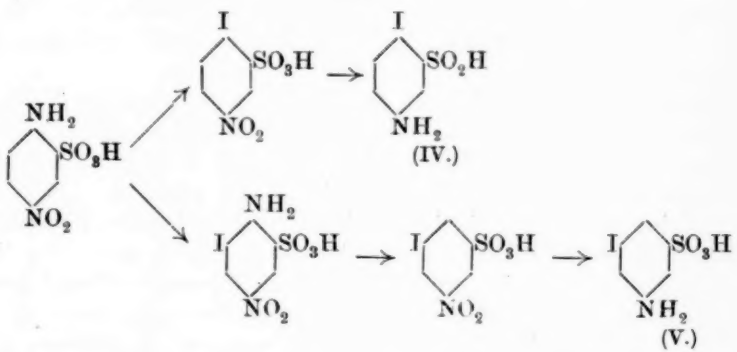
6-*Iodoaniline-2-sulphonic acid* (III) was prepared with more difficulty, and small quantities only have been obtained. The *p*-nitroaniline-*o*-sulphonic acid described in 1911 (T., **99**, 325) gave, when treated with iodine chloride, an iodo-derivative, for which only one configuration is possible. Reduction of the nitro-group gave a diaminosulphonic acid, which, by the loss of one amino-

group, could yield two different iodoanilinesulphonic acids, as figured below:

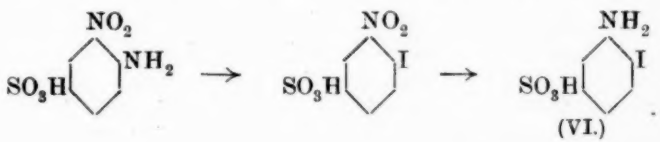


Considerations of steric hindrance would suggest the first as the more probable reaction, and that it does take place exclusively is proved by the conversion of the iodoanilinesulphonic acid into the well-known 2:3-di-iodobenzenesulphonic acid.

4-*Iodoaniline*-3-*sulphonic acid* (IV) and 5-*iodoaniline*-3-*sulphonic acid* (V) were both obtained from *p*-nitroaniline-*o*-sulphonic acid by submitting it to the following series of reactions:



6-*Iodoaniline*-3-*sulphonic acid* (VI) was obtained by a similar series of reactions from *o*-nitroaniline-*p*-sulphonic acid.



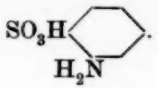
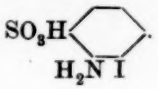
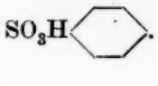
These acids resemble each other in appearance, being well characterised, colourless substances crystallising from water in needles. They vary somewhat in solubility in water, the 6-iodo-

aniline-2-sulphonic acid being readily soluble, most of the others giving $N/32$—$N/64$-solutions, and 3-iodoaniline-4-sulphonic acid dissolving sparingly. The latter acid crystallises with one molecule of water; the rest are anhydrous.

In the experiments on conductivities, the main difficulty experienced was in the accurate determination of the strength of the acid solution. The unsubstituted anilinesulphonic acids were first investigated, the pure acids being either (1) weighed out to the required strength, or (2) titrated with standard alkali and diluted to the required strength; the two methods were found to give identical results when special precautions in the standardisation of materials were taken. The numbers obtained in the case of the three anilinesulphonic acids are all higher than the corresponding numbers obtained by Ostwald (*Zeitsch. physikal. Chem.*, 1889, **3**, 106), Winkelblech (*ibid.*, 1901, **36**, 546), White and Jones (*Amer. Chem. J.*, 1909, **42**, 520), and Wheeler and Jones (*ibid.*, 1910, **44**, 159). It is to be noted, however, that these higher values give a better dissociation constant than do the earlier and lower ones. For example, for aniline-*p*-sulphonic acid, Ostwald gives a mean $K=5{\cdot}81\times10^{-4}$, showing a maximum variation of $0{\cdot}8\times10^{-5}$, Winkelblech a mean $K=6{\cdot}2\times10^{-4}$ with a variation of $2{\cdot}3\times10^{-5}$, Wheeler and Jones a mean $K=6{\cdot}55\times10^{-4}$ and variation $1{\cdot}7\times10^{-5}$, and the author a mean $K=7{\cdot}05\times10^{-4}$ with a variation of $0{\cdot}6\times10^{-5}$.

For aniline-*o*-sulphonic acid, the mean value $K=4{\cdot}29\times10^{-3}$, as against Ostwald's $K=3{\cdot}21\times10^{-3}$, and for aniline-*m*-sulphonic acid the value $K=2{\cdot}11\times10^{-4}$, as against Ostwald's $K=1{\cdot}85\times10^{-4}$ and Wheeler and Jones' $K=1{\cdot}97\times10^{-4}$, have been obtained.

The introduction of iodine into the nucleus increases the conductivities of the acids very considerably, bringing them into the category of strong acids, which do not obey Ostwald's dilution law; in the case of some of the aniline-*m*-sulphonic acids only can a value of K which is even approximately constant be obtained. It is the position of the iodine relative to the amino-group which is the determining factor; whether in the meta- or para-position the effect in increasing the strength of the acid is approximately the same, but when in the ortho-position the effect is very marked. The influence of the amino-group in diminishing the strength of the sulphonic acid is almost entirely neutralised by the ortho-substituted iodine, and the iodoamino-sulphonic acid is found to conduct to the same extent as benzenesulphonic acid itself. A comparison of 6-iodoaniline-2-sulphonic acid with aniline-*o*-sulphonic acid and with benzenesulphonic acid shows this clearly.

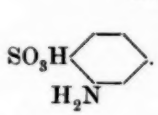
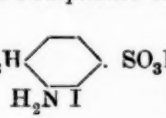
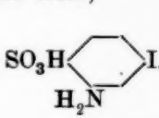
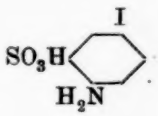




v.	λ_v.	λ_v.	λ_v.
32	109·5	—	321·07
64	144·1	340·0	—
128	183·4	348·2	350·47
256	225·8	353·1	—
512	265·0	356·7	356·38
1024	299·5	357·8	359·03
2048	—	—	354·22

The figures for benzenesulphonic acid are those given by Wightman and Jones (*Amer. Chem. J.*, 1911, **46**, 56).

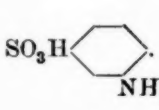
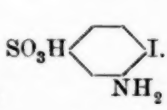
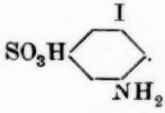
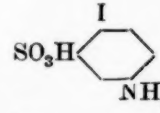
The three following tables give the conductivities of the iodo-substituted acids side by side with those of the unsubstituted acid from which they are derived.

Aniline-o-*sulphonic Acid*,

v.	λ_v.	λ_v.	λ_v.	λ_v.
32	109·5	—	—	—
64	144·1	340·0	—	—
128	183·4	348·2	309·5	289·6
256	225·8	353·1	333·2	320·9
512	265·0	356·7	348·7	341·6
1024	299·5	357·8	357·4	355·0

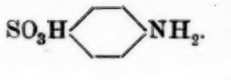
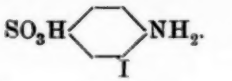
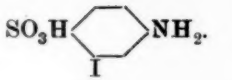
Aniline-m-*sulphonic Acid*,

v.	λ_v.	λ_v.	λ_v.	$K\times10^4$.	λ_v.	$K\times10^4$.
32	28·15	—	—	—	—	—
64	39·12	242·3	115·3	23·5	73·98	8·30
128	54·01	286·4	149·5	23·0	99·14	8·15
256	73·98	319·3	191·2	23·5	130·2	8·02
512	99·28	342·2	235·5	24·1	167·8	7·94
1024	131·5	358·2	279·9	—	210·4	8·00
	$K=$		$K=$		$K=$	
	$2{\cdot}11\times10^{-4}$.		$23{\cdot}5\times10^{-4}$.		$8{\cdot}08\times10^{-4}$.	

Ostwald's value $\lambda_\infty = 356$ has been used in calculating the dissociation constants of the anilinesulphonic acids, and $\lambda_\infty = 360$ for calculating those of the iodoanilinesulphonic acids.

Aniline-p-sulphonic Acid.

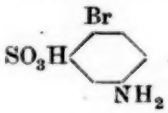
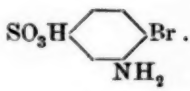




v.	λ_v.	λ_v.	λ_v.
32	49·73	266·7	—
64	68·30	301·9	—
128	92·54	329·5	—
256	122·9	347·4	228·7
512	159·4	360·0	268·4
1024	200·7	366·2	302·7

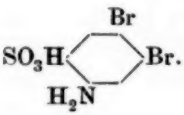
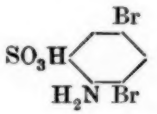
The same screening of the amino-group is brought about by other groups than iodine, for example, bromine, the nitro-group, hydroxy-group, etc., although none is quite so effective as iodine. From the literature on the subject of conductivities of acids, the following data have been selected as bearing out what has been shown to be true of iodo-substituted acids.

Bromo-derivatives of Anilinesulphonic Acids.

The acid containing bromine in the ortho-position with respect to the amino-group has a greater conductivity at all dilutions than the one with bromine in the para-position.

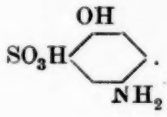



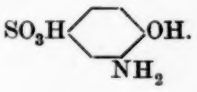
v.	λ_v.	λ_v.
64·0	70·0	—
73·5	—	224·4
128·0	92·3	—
147·0	—	351·8
256·0	122·5	—
294·0	—	276·5
512·0	157·4	—
588·0	—	296·3
1024·0	197·5	—
1176·0	—	312·6

v.	λ_v.	λ_v.
109·8	—	338
219·6	—	343
278·0	338	—
439·2	—	346
556·0	346	—
878·4	—	348
1112·0	351	—

Hydroxy-derivatives of Anilinesulphonic Acids.



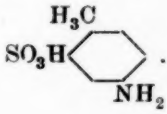


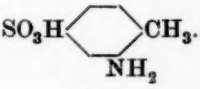
v.	λ_v.	λ_v.
64	—	26·5
128	—	36·9
256	16·0	51·0
512	22·4	69·8
1024	31·3	125·0

Here the same thing is observed, although both acids have a smaller conductivity than the unsubstituted metanilic acid.

Alkyl Derivatives of Anilinesulphonic Acids.

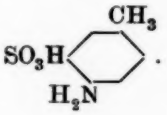
The introduction of methyl into aniline-*m*-sulphonic acid gives results in harmony with the above.

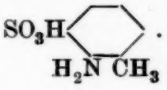




v.	λ_v.	λ_v.
32	12·6	—
64	17·7	42·3
128	24·7	56·8
256	34·5	77·2
512	47·7	104·6
1024	—	137·5

In the case of aniline-*o*-sulphonic acid, however, the position of the substituted group in the nucleus seems to make practically no difference to the conductivity value.

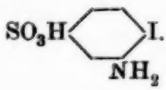


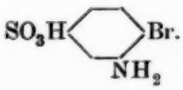


v.	λ_v.	λ_v.
32	53·9	51·0
64	73·7	69·9
128	99·5	94·6
256	131·4	125·2
512	169·1	162·5
1024	210·9	—

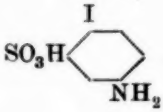
Halogen Derivatives of Anilinesulphonic Acids.

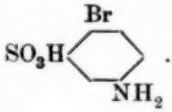
Iodine is more effective than bromine in neutralising the effect of the amino-group, and bromine than chlorine. This is seen from a consideration of the three following tables:



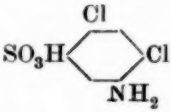


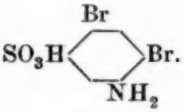
v.	λ_v.	λ_v.
64·0	243·3	—
73·5	[—	224·4
128·0	286·4	—
147·0	—]	251·8
256·0	319·3	—
294·0	—	276·5
512·0	342·2	—
588·0	—	296·3
1024·0	358·2	—
1176·0	—	312·6





v.	λ_v.	λ_v.
64·0	73·98	70·0
128·0	99·14	92·3
256·0	130·2	122·5
512·0	167·8	157·4
1024·0	210·4	197·5





v.	λ_v.	λ_v.
64·0	—	—
71·9	—	262
128·0	130·0	—
143·8	—	289
256·0	158·4	—
287·6	—	313
512·0	189·2	—
575·2	—	329
1024·0	227·9	—
1150·0	—	340
2048·0	268·5	—

Experimental.

Preparation of the Acids.

4-Iodoaniline-2-sulphonic acid was prepared from aniline-*o*-sulphonic acid according to the method previously described (T., 1909, **95**, 1698). After repeated crystallisations, the acid still possessed a faint violet tinge (Found: C = 24·03; H = 1·99. Calc.: C = 24·07; H = 2·00 per cent.).

Solubility.—One hundred grams of water dissolve 0·51 gram of the acid at 25°.

5-*Iodoaniline-2-sulphonic Acid.*—The method of preparation consists in (a) introducing iodine into *p*-nitroaniline-*m*-sulphonic acid, (*b*) displacing the amino-group by hydrogen, (*c*) reducing the nitro-group.

(a) *Preparation of* 6-*Iodo*-4-*nitroaniline*-2-*sulphonic Acid.*—Fifteen grams of 4-nitroaniline-3-sulphonic acid, prepared by Eger's method from aniline-*m*-sulphonic acid (*Ber.*, 1888, **21**, 2581), were dissolved in a large volume of boiling water, a little hydrochloric acid was added, and 11·2 grams of iodine chloride were then passed into the solution, which was kept at 90—95°. Experiments were carried out at lower temperatures, but the sparing solubility of the acid enabled only small quantities to be worked up at a time, and the yield was only inappreciably increased. The reddish-yellow solution, after remaining for half an hour, was evaporated to a very small bulk, when the dark yellow acid separated on cooling. A yield of 20·4 grams, amounting to 87 per cent. of the theoretical, was obtained.

(b) *Preparation of* 4-*Iodo*-2-*nitrobenzenesulphonic Acid.*—Fifteen grams of the above acid were diazotised in sulphuric acid solution by means of 3 grams of sodium nitrite. The sparingly soluble diazo-compound was then boiled with alcohol under a reflux condenser, and the dark-coloured residue, after removing the alcohol, was dissolved in water, neutralised with sodium carbonate and boiled with animal charcoal; the yellow filtrate deposited, on concentration, long, yellow needles, which became opaque on exposure to air. The yield amounted to nearly 70 per cent. of the theoretical.

(c) *Preparation of* 5-*Iodoaniline*-2-*sulphonic Acid.*—The nitro-acid was reduced, as usual, with stannous chloride at 100°. There was little apparent action, the solution retaining its yellow colour, but when the yellow solid which was precipitated on cooling was dissolved in sodium carbonate, a white amino-acid was obtained

from this solution by adding concentrated acid. Proof of its structure was obtained by replacing the amino-group by iodine and converting the di-iodobenzenesulphonic acid into a chloride melting at 75°, and identical with 2:4-di-iodobenzenesulphonyl chloride:

0·1341 gave 0·1181 CO_2 and 0·0248 H_2O. C = 24·01; H = 2·05.
$C_6H_6O_3NIS$ requires C = 24·07; H = 2·00 per cent.

Solubility.—One hundred grams of water contain 0·26 gram of acid at 25°.

6-*Iodoaniline*-2-*sulphonic Acid.*—6-Iodo-4-nitroaniline-2-sulphonic acid (T., 1911, **99**, 330) was reduced with stannous chloride at 100° to 6-*iodo*-p-*phenylenediamine*-2-*sulphonic acid*, which is a white, crystalline substance sparingly soluble in water. A small quantity (2·5 grams) was diazotised in the minimum amount of sulphuric acid by adding 0·55 gram of sodium nitrite (theoretical amount for one amino-group is 0·53 gram); the dark yellow diazo-compound was then collected and boiled with alcohol. After evaporating off the alcohol and boiling the neutralised residue with animal charcoal, the filtered solution and the amino-acid precipitated from it were still somewhat coloured. This amino-acid has not yet been obtained in a colourless condition; it crystallises in pale brown needles from water, in which it is rather readily soluble. Its conversion into 2:3-di-iodobenzenesulphonyl chloride, melting at 127°, confirmed its constitution:

0·1937 gave 0·1701 CO_2 and 0·0370 H_2O. C = 23·95; H = 2·11.
$C_6H_6O_3NIS$ requires C = 24·07; H = 2·00 per cent.

4-*Iodoaniline*-3-*sulphonic Acid.*—Nineteen grams of *p*-nitroaniline-*o*-sulphonic acid (T., 1911, **99**, 324) were diazotised in sulphuric acid solution by 5·7 grams of sodium nitrite, and the bright yellow diazo-compound was decomposed by potassium iodide. A voluminous yellow precipitate of potassium 2-iodo-5-nitrobenzenesulphonate separated at once from the hot solution, and was collected and well washed with cold water. This salt was suspended in concentrated hydrochloric acid and reduced with stannous chloride, the completion of the reduction being readily ascertained by the change in colour and in the appearance of the crystalline product. The amino-acid was purified, as usual, by precipitating it with concentrated acid from its solution in sodium carbonate. It separates from a concentrated aqueous solution in small, sparkling crystals, from more dilute solutions in fine, transparent needles. Its conversion into 2:5-di-iodobenzenesulphonyl chloride, melting at 132°, afforded proof of its constitution:

0·1871 gave 0·1644 CO_2 and 0·0331 H_2O. C = 23·96; H = 1·97.
$C_6H_6O_3NIS$ requires C = 24·07; H = 2·00 per cent.

Solubility.—One hundred grams of water contain 1·36 grams of anhydrous acid at 25°.

5-*Iodoaniline*-3-*sulphonic acid* was prepared from *p*-nitroaniline-*o*-sulphonic acid through 6-iodo-4-nitroaniline-2-sulphonic acid by (1) removing the amino-group, (2) reducing the nitro-group. When the diazo-compound was boiled with alcohol, nitrogen was evolved rapidly, and, after about forty-five minutes, a clear, pale yellow solution was obtained, from which, on concentration, pale yellow crystals separated; these were neutralised with sodium carbonate, and the sodium salt was recrystallised. *Sodium* 3-*iodo*-5-*nitrobenzenesulphonate* was dissolved in hydrochloric acid and reduced with stannous chloride at 100°; precipitation of the amino-acid as a cream-coloured, crystalline mass followed almost immediately. The acid, dissolved in alkali and reprecipitated by mineral acid, was then repeatedly crystallised from hot water, separating in fine, white needles:

0·1778 gave 0·1569 CO_2 and 0·0326 H_2O. C = 24·07; H = 2·03.
$C_6H_6O_3NIS$ requires C = 24·07; H = 2·00 per cent.

Solubility.—One hundred grams of water dissolve 1·31 grams of anhydrous acid at 25°.

The constitution of the acid was established by replacing the amino-group by iodine and converting the resulting di-iodobenzenesulphonic acid into 3:5-di-iodobenzenesulphonyl chloride, which crystallised from ether in needles melting at 93°.

6-*Iodoaniline*-3-*sulphonic Acid*.—*o*-Nitroaniline-*p*-sulphonic acid was prepared (1) by nitrating sulphanilic acid according to Nietzki's method (*Ber*., 1885, **18**, 294), (2) by sulphonating *o*-nitroaniline by Hardtung's method (*Annalen*, 1881, **206**, 96). After displacing the amino-group by iodine, and subsequently reducing the nitro-group, the iodoaminosulphonic acid was obtained as a grey powder, which crystallised from a large bulk of water:

0·2075 gave 0·1833 CO_2 and 0·0388 H_2O. C = 24·09; H = 2·07.
$C_6H_6O_3NIS$ requires C = 24·07; H = 2·00 per cent.

Solubility.—One hundred grams of water contain 0·48 gram of acid at 25°.

2-Iodoaniline-4-sulphonic acid was prepared as previously described (T., 1909, **95**, 1693) (Found: C = 24·03; H = 2·11. Calc.: C = 24·07; H = 2·00 per cent.).

Solubility.—One hundred grams of water dissolve 2·07 grams of the anhydrous acid at 25°.

3-Iodoaniline-4-sulphonic acid was prepared by reducing 2-iodo-4-nitrobenzenesulphonic acid (T., 1909, **95**, 1708) by means of stannous chloride. The reduction proceeded rapidly on the water-bath, and was complete in less than an hour. The iodoamino-acid, precipitated from its solution in alkali by concentrated mineral acid, was recrystallised from water several times, separating in fine, transparent needles containing one molecule of water of crystallisation:

0·1861 gave 0·1552 CO_2 and 0·0425 H_2O. C = 22·74; H = 2·53.
$C_6H_6O_3NIS,H_2O$ requires C = 22·71; H = 2·52 per cent.

Solubility.—One hundred grams of water dissolve 0·194 gram of anhydrous acid at 25°.

Conductivity experiments were carried out in Ostwald cells in a thermostat at 25°. An ordinary Wheatstone bridge, carefully calibrated, and standard resistances were employed. The conductivity water was obtained by distilling first with acid, then with alkaline permanganate, finally alone, in the ordinary form of apparatus, consisting of tin distilling flask, block-tin condenser, and Jena-glass receiver. In making the solution of the acid for conductivity measurements, excess of the acid was shaken vigorously in a Jena-glass flask with conductivity water and allowed to remain for some time. The solid was then filtered off and the filtrate titrated against standard sodium hydroxide of slightly less strength; the solution was then diluted to that strength. Standard flasks, pipettes, and burettes were used throughout.

In the preparation of the standard solutions, conductivity water was used throughout. $N/10$-Sodium hydroxide was titrated against $N/10$-hydrochloric acid which had previously been standardised by means of pure sodium carbonate, and each solution was then diluted to $N/32$, $N/64$, $N/128$, $N/256$, and titrations of one against the other were carried out in order that errors introduced by the hydrolysis of the indicator, phenolphthalein, at such considerable dilutions should be obviated. The results of experiments carried out under these conditions agreed well with those obtained by weighing out the acid directly and dissolving it in the requisite amount of water. After one set of results had been obtained, the acid was recrystallised and the conductivity again determined; the recrystallisations and subsequent determination of conductivity were repeated until consecutive experiments gave identical results; in this way, the purity of the acid was guaranteed. In some cases,

ten crystallisations had to be carried through before satisfactorily concordant results were obtained.

Further experiments on the conductivities of the anilinesulphonic acids are being carried out, and it is hoped that the results may shortly be ready for publication.

I wish to express my thanks to Miss E. E. Field for valuable help given during the course of this investigation.

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FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

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$C_3H_6O_2$ Methyl acetate, rate of hydrolysis of, by hydrochloric acid (BURROWS), 1230.

Propionic acid, silver salt, solubility of, in propionic acid (KNOX and WILL), 853.

$C_3H_7N_5$ Substance, from oxidation of thiocarbamide with permanganate (WERNER), 1173.

$C_3H_8O_3$ Glycerol, and its nitric esters, absorption spectra of (HEPWORTH), 840.

3 III

$C_3H_4ON_2$ Cyanoacetamide, condensation of ketones with (KON and THORPE), 686.

$C_3H_8N_2S$ Ethyl*iso*thiocarbamide, and its picrate (WERNER), 1172.

C_4 Group.

C_4H_8 β-Butylene, preparation of (KING), 1406.

4 II

$C_4H_6O_6$ Tartaric acid, rotation dispersion of alkyl esters of (FRANKLAND and GARNER), 636.

$C_4H_6N_2$ 2-Methylglyoxaline, and its salts (FARGHER and PYMAN), 231.

C_4H_8O Methyl ethyl ketone, preparation of, from *n*-butyl alcohol (KING), 1404; vapour pressure and density of mixtures of acetone and (PRICE), 1116.

$C_4H_{10}O$ *n*-Butyl alcohol, pure, preparation of, and the detection of impurity in it (ORTON and JONES), 1194.

Ethyl ether, ignition of mixtures of alcohol, air and (WHITE and PRICE), 1462.

$C_4H_{10}S$ Ethyl sulphide, reactions of, with mercuric iodide and alkyl iodides (RÂY and GUHA), 1154.

$C_4H_{11}N$ Butylamine, preparation of (WERNER), 1010.

4 III

$C_4H_5O_3N_3$ Nitromethylglyoxalines (FARGHER and PYMAN), 234.

$C_4H_7ON_3$ Alacreatine, preparation of, and its salts (FARGHER and PYMAN), 253.

$C_4H_8O_7N_2$ Glyceryl methyl ether dinitrate (JONES), 76.

4 IV

C_4H_4NClS 2-Chloro-4-methylthiazole (TCHERNIAC), 1072.

C_4H_5ONS α-, β-, and *iso*-Methylrhodim (TCHERNIAC), 1075.

Thiocyanoacetone, and its isomerides (TCHERNIAC), 1071.

C_5 Group.

$C_5H_8N_2$ 4:5-Dimethylglyoxaline, and its hydrochloride (FARGHER and PYMAN), 233.

$C_5H_{10}N_2$ Diazo*iso*pentane (WERNER), 1101.

$C_5H_{12}O$ Amyl alcohol, use of, as a membrane (DONNAN and GARNER), 1313.

5 III

$C_5H_4O_4N_2$ Glyoxaline-4:5-dicarboxylic acid, preparation of, and its sodium salt (FARGHER and PYMAN), 227.

$C_5H_5O_4N_3$ 2-Aminoglyoxaline-4:5-dicarboxylic acid (FARGHER and PYMAN), 259.

$C_5H_6O_2N_2$ 2-Methylglyoxaline-4-carboxylic acid, and its salts (FARGHER and PYMAN), 230.
$C_5H_7ON_3$ 2-Acetylaminoglyoxaline (FARGHER and PYMAN), 248.
$C_5H_7O_2N$ Ethyl cyanoacetate, condensation of ketones with (KON and THORPE), 686.
$C_5H_{11}O_2N_3$ Nitroso-*n*-butylurea (WERNER), 1101.
$C_5H_{12}ON_2$ *n*-Butylurea (WERNER), 1101.

5 IV

$C_5H_2ON_6Fe$ Nitroprussic acid, alkali and methylammonium salts (BURROWS and TURNER), 1429.
$C_5H_5ON_2Cl$ Glyoxaline-4-acetyl chloride, hydrochloride of (FARGHER and PYMAN), 1019.
C_5H_7ONS Dimethylrhodim (TCHERNIAC), 1076.

C_6 Group.

$C_6H_4O_4$ Substance, from acetic anhydride and aconitic acid (TAYLOR), 889.
$C_6H_6O_6$ Aconitic acid, presence of, in sugar-cane juices, and its detection (TAYLOR), 886.
$C_6H_6S_2$ 2:5-Dimethylthiën (TCHERNIAC), 1085.
$C_6H_{10}N_2$ 2:4:5-Trimethylglyoxaline, and its picrate (FARGHER and PYMAN), 233.

6 III

$C_6H_4N_6Fe$ Ferrocyanic acid, copper salt, use of, as a membrane (DONNAN and GARNER), 1313.
C_6H_5ClS *p*-Chlorophenyl mercaptan, reaction of, with mercuric nitrite (RÂY and GUHA), 1154.
$C_6H_6O_3Se$ Phenylselenious acid, preparation of, and its sodium salt (PYMAN), 167.
$C_6H_6O_4Se$ Phenylselenic acid, and its salts (PYMAN), 169.
$C_6H_8O_2N_2$ 2-Ethylglyoxaline-4-carboxylic acid, and its picrate (FARGHER and PYMAN), 1017.
$C_6H_{11}O_3N$ 4-Hydroxyhygric acid (GOODSON and CLEWER), 926.
$C_6H_{13}ON$ Diacetonamine, preparation and reactions of (EVEREST), 588.
$C_6H_{13}O_2N_3$ Nitroso*iso*amylurea (WERNER), 1101.

6 IV

$C_6H_5O_4NSe$ *m*-Nitrophenylselenious acid (PYMAN), 169.
$C_6H_5O_5NSe$ *m*-Nitrophenylselenic acid, and its salts (PYMAN), 170.
$C_6H_7O_3NSe$ *m*-Aminophenylselenic acid, and its sodium salt (PYMAN), 175.

6 V

$C_6H_6O_3NIS$ Iodoanilinesulphonic acids, conductivity of (BOYLE), 1505.

C_7 Group.

C_7H_8 Toluene, determination of purity of (ORTON and JONES), 1055; commercial, estimation of the purity of (LUMSDEN), 1366.

7 II

C_7H_9N Methylaniline, preparation of (FRANKLAND, CHALLENGER, and NICHOLLS), 198.
C_7H_9S *p*-Tolyl mercaptan, reaction of, with mercuric nitrite (RÂY and GUHA), 1152.
$C_7H_{12}O_2$ *cyclo*Hexanecarboxylic acid, preparation of (INGOLD and THORPE), 376.

7 III

$C_7H_{10}O_2N_2$ Ethyl 2-methylglyoxaline-4-carboxylate (FARGHER and PYMAN), 1017.

$C_7H_{13}O_3N$ Betonicine, and its salts (GOODSON and CLEWER), 932.

Turicine, and its salts (GOODSON and CLEWER), 931.

7 IV

$C_7H_6O_5NAs$ 1:2-Dihydrobenzoxazolone-4-arsinic acid (FARGHER), 991.

$C_7H_6O_5N_2As$ 5-Nitro-6-amino-*m*-tolylarsinic acid (FARGHER), 989.

$C_7H_7O_3N_2As$ 1:3-Benzodiazolearsinic acids (BAXTER and FARGHER), 1372.

$C_7H_8O_3N_3As$ 7-Methyl-1:2:3-benzotriazole-5-arsinic acid (BAXTER and FARGHER), 1378.

$C_7H_{11}O_2N_2As$ 5:6-Diamino-*m*-tolylarsinic acid (BAXTER and FARGHER), 1377.

C_8 Group.

$C_8H_{12}O_4$ *cyclo*Hexane-1:1-dicarboxylic acid (INGOLD and THORPE), 376.

$C_8H_{12}O_6$ γ-Methylbutane-αβδ-tricarboxylic acid, preparation of (THORPE), 684.

$C_8H_{16}O_5$ Dimethyl methylarabinoside (IRVINE and DICK), 599.

$C_8H_{19}N$ *n*-Dibutylamine, preparation of (WERNER), 1010.

8 III

$C_8H_7O_4Br$ Bromotsuginic acid (MANNING and NIERENSTEIN), 664.

$C_8H_9O_2N_3$ Nitrosobenzylurea (WERNER), 1101.

$C_8H_9N_3S_2$ Dithiazylamine, and its hydrochloride (TCHERNIAC), 1082.

$C_8H_{10}ON_2$ α-Cyano-Δ^1-*cyclo*penteneacetamide (KON and THORPE), 697.

$C_8H_{12}O_2N_2$ Ethyl 2-ethylglyoxaline-4-carboxylate (FARGHER and PYMAN), 1018.

$C_8H_{12}O_3N_2$ Ethyl α-hydroxy-β-glyoxaline-4-propionate (FARGHER and PYMAN), 1020.

$C_8H_{13}O_2N$ Oscine, and its salts, resolution of (KING), 476.

$C_8ON_6S_2$ Substance, from chloropicrin and the potassium salt of 2:5-dithiol-1:3:4-thiodiazole (RÂY, GUHA, and DAS), 1312.

8 IV

$C_8H_9O_3NSe$ *m*-Acetylaminophenylselenious acid, and its sodium salt (PYMAN), 173.

$C_8H_9O_3N_2As$ Methyl-1:3-benzodiazole-5-arsinic acids (BAXTER and FARGHER), 1377.

$C_8H_9O_4NSe$ *m*-Acetylaminophenylselenic acid, salts of (PYMAN), 174.

C_9 Group.

$C_9H_8O_2$ Atropic acid, preparation of (MCKENZIE and WOOD), 834.

Cinnamic acid, molecular refractivity of derivatives of (WALKER and JAMES), 1243.

$C_9H_8N_2$ 2-Phenylglyoxaline, preparation of, and its salts (FARGHER and PYMAN), 232.

$C_9H_8N_4$ Benzeneazoglyoxaline (FARGHER and PYMAN), 237.

$C_9H_{10}O_3$ Atrolactinic acid, preparation of (MCKENZIE and WOOD), 833.

ω-Hydroxy-*m*-tolylacetic acid (GOUGH and THORPE), 1162.

Tropic acid, and its salts, resolution of (KING), 476.

Tropic acids, preparation of (MCKENZIE and WOOD), 828.

$C_9H_{10}N_4$ 2-Amino-4-*p*-aminophenylglyoxaline, and its salts (FARGHER and PYMAN), 239.

$C_9H_{12}O_3$ *cyclo*Pentane-1:1-diacetic anhydride (KON and THORPE), 700.

$C_9H_{14}O_3$ β-Methyl-β-*iso*propylglutaric anhydride (Kon and Thorpe), 702.
$C_9H_{14}O_4$ *cyclo*Pentane-1:1-diacetic acid, and its silver salt (Kon and Thorpe), 700.
$C_9H_{14}O_7$ Trimethylsaccharolactone (Haworth and Leitch), 816.
$C_9H_{16}O_4$ β-Methyl-β-*iso*propylglutaric acid (Kon and Thorpe), 702.

9 III

$C_9H_7N_4Br$ 2- and 4-*p*-Bromobenzeneazoglyoxalines (Fargher and Pyman), 243.
C_9H_8NBr ω-Bromo-*m*-tolylacetonitrile (Gough and Thorpe), 1161.
C_9H_9ON ω-Hydroxy-*m*-tolylacetonitrile (Gough and Thorpe), 1162.
$C_9H_9O_2Cl$ β-Chlorohydratropic acid, preparation of (McKenzie and Wood), 835.
$C_9H_9O_4Br$ Methyl bromotsuginate (Manning and Nierenstein), 664.
$C_9H_9N_4Br$ 2-5′-Bromo-2′-aminoanilinoglyoxaline (Fargher and Pyman), 246.
$C_9H_{10}ON_2$ Base, from reduction of 5-benzeneazo-4-methylglyoxaline (Fargher and Pyman), 253.
$C_9H_{13}O_2N$ Imide of *cyclo*pentane-1:1-diacetic acid (Kon and Thorpe), 700.
$C_9H_{20}ON_2$ *as*-Dibutylcarbamide (Werner), 1014.

9 IV

$C_9H_{10}O_6NAs$ 6-Oxalylamino-*m*-tolylarsinic acid (Fargher), 989.
$C_9H_{10}O_7NAs$ 5-Nitro-6-hydroxy-*m*-tolylarsinic acid (Fargher), 990.
$C_9H_{11}O_3N_2As$ 2:7-Dimethyl-1:3-benzodiazole-5-arsinic acid (Baxter and Fargher), 1379.
$C_9H_{18}ONCl$ Dibutylcarbamyl chloride (Werner), 1013.

C_{10} Group.

$C_{10}H_8O_3$ Aldehyde, from hemlock tannin (Manning and Nierenstein), 668.
$C_{10}H_8O_4$ Acid, and its salts, from oxidation of aldehyde from hemlock tannin (Manning and Nierenstein), 668.
$C_{10}H_8S$ α-Naphthyl mercaptan, reaction of, with mercuric nitrite (Rây and Guha), 1150.
$C_{10}H_9N$ β-Naphthylamine, formation of diazoamino-compounds from (Norman), 673.
$C_{10}H_{10}N_4$ Benzeneazo-4-methylglyoxalines (Fargher and Pyman), 249.
$C_{10}H_{12}O_3$ Ethyl *l*-mandelate, catalytic racemisation of (McKenzie and Wren), 602.
$C_{10}H_{12}N_4$ 2-Amino-5-*p*-aminophenyl-4-methylglyoxaline, and its salts (Fargher and Pyman), 250.
$C_{10}H_{13}N$ Neomethylhydrindamines, optically active, and their salts (Harris), 61.
$C_{10}H_{14}O_2$ Glycol *o*- and *m*-xylyl ethers (Boyd and Thomas), 1243.
$C_{10}H_{14}N_2$ Nicotine, physical constants of (Jephcott), 104.
$C_{10}H_{16}O_4$ 2-Methyl*cyclo*pentane-1:1-diacetic acid (Kon and Thorpe), 697.

10 III

$C_{10}H_7O_3N$ 4-Nitro-β-naphthol (Morgan and Evens), 1132.
$C_{10}H_7O_4N_3$ 2:4-Dinitro-α-naphthylamine, preparation of (Morgan and Evens), 1128.
$C_{10}H_8O_2N_2$ 2-Phenylglyoxaline-4-carboxylic acid (Fargher and Pyman), 1018.
$C_{10}H_9ON_3$ 2-Benzoylaminoglyoxaline (Fargher and Pyman), 248.
Glyoxaline-4-carboxyanilide (Fargher and Pyman), 228.

$C_{10}H_9O_5Br$ Acetyl derivative of bromotsuginic acid (MANNING and NIERENSTEIN), 664.

$C_{10}H_9N_4Br$ 4-*p*-Bromobenzeneazo-2-methylglyoxaline (FARGHER and PYMAN), 256.

$C_{10}H_{11}ON_3$ Base, from reduction of 5-benzeneazo-4-methylglyoxaline (FARGHER and PYMAN), 255.

$C_{10}H_{11}O_4Br$ Ethyl bromotsuginate (MANNING and NIERENSTEIN), 664.

10 IV

$C_{10}H_8O_2N_2S_3$ Substance, from chloroacetic acid and the potassium salt of 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole (RÂY, GUHA, and DAS), 1312.

$C_{10}H_9N_2BrS_3$ Substance, from ethylene bromide and the potassium salt of 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole (RÂY, GUHA, and DAS), 1312.

$C_{10}H_{13}O_5N_2As$ 3:4-Diacetylaminophenylarsinic acid (BAXTER and FARGHER), 1376.

C_{11} Group.

$C_{11}H_9N$ Indenyl-3-acetonitrile (INGOLD and THORPE), 152.

$C_{11}H_{10}O_4$ Ethyl ester of acid, from hemlock tannin (MANNING and NIERENSTEIN), 668.

$C_{11}H_{11}N$ β-Naphthylmethylamine, preparation of (MORGAN and EVANS), 1140.

$C_{11}H_{12}O_4$ β-ω-Carboxy-*m*-tolylpropionic acid, and its salts (GOUGH and THORPE), 1164.

$C_{11}H_{14}O_3$ 5-*cyclo*Hexane*spiro*di*cyclo*pentan-3-one-1-carboxylic acid (INGOLD and THORPE), 364.

$C_{11}H_{14}O_3$ *cyclo*Pentane-1:1-dimalonic acid (KON and THORPE), 700.

$C_{11}H_{16}O_2$ Glycol mesityl ether (BOYD and THOMAS), 1243.

$C_{11}H_{16}O_3$ 5-*cyclo*Hexane*spirocyclo*pentan-3-one-1-carboxylic acid (INGOLD and THORPE), 372.

$C_{11}H_{18}O_3$ 5-*cyclo*Hexane*spirocyclo*pentan-3-ol-1-carboxylic acid (INGOLD and THORPE), 373.

$C_{11}H_{18}O_4$ 2-Methyl*cyclo*hexane-1:1-diacetic acid, and its silver salt (KON and THORPE), 694.

$C_{11}H_{18}N_2$ Tolylene-4-*N*-*n*-butyldiamines, and their hydrochlorides (REILLY and HICKINBOTTOM), 176.

11 III

$C_{11}H_9O_3N$ 4-Nitro-β-naphthyl methyl ether (MORGAN and EVENS), 1133.

$C_{11}H_{10}ON_2$ 1-Nitroso-β-naphthylmethylamine (MORGAN and EVANS), 1141.

$C_{11}H_{11}ON_3$ 2-Methylglyoxaline-4-carboxyanilide (FARGHER and PYMAN), 230.

$C_{11}H_{11}O_2N$ β-ω-Cyano-*m*-tolylpropionic acid (GOUGH and THORPE), 1164.

$C_{11}H_{11}O_2N_3$ ω-Imide-αα′-dicyano*cyclo*pentane-1:1-diacetic acid (KON and THORPE), 701.

$C_{11}H_{11}O_2Cl$ Ethyl α-chlorocinnamates (WALKER and JAMES), 1247.

$C_{11}H_{12}O_4N_2$ ω-Di-imide of *cyclo*pentane-1:1-dimalonic acid (KON and THORPE), 699.

$C_{11}H_{13}ON$ ω-Ethoxy-*m*-tolylacetonitrile (GOUGH and THORPE), 1163.

$C_{11}H_{13}O_3N_3$ ω-Imide of αα′-dicyano-β-methyl-β-*iso*propylglutaric acid (KON and THORPE), 702.

$C_{11}H_{14}O_2N_4$ ω-Di-iminodi-imide of *cyclo*pentane-1:1-dimalonic acid ($+\frac{1}{2}H_2O$) (KON and THORPE), 698.

$C_{11}H_{12}O_4N_2$ ω-Imide of *aa'*-dicarbamyl*cyclo*pentane-1:1-diacetic acid (KON and THORPE), 701.

$C_{11}H_{17}O_7N$ Amide of *cyclo*pentane-1:1-dimalonic acid (KON and THORPE), 699.

11 IV

$C_{11}H_9O_7N_4S$ 2-*p*-Sulphobenzeneazoglyoxaline-4:5-dicarboxylic acid ($+2H_2O$), and its sodium salt (FARGHER and PYMAN), 258.

C_{12} Group.

$C_{12}H_{10}$ Diphenyl, preparation of (KRIZEWSKY and TURNER), 559.

12 II

$C_{12}H_{10}N_2$ Harman, preparation of, and its salts (PERKIN and ROBINSON), 971.

$C_{12}H_{11}N$ α-Indenyl-2- and -3-propionitriles (INGOLD and THORPE), 153.

$C_{12}H_{12}O_4$ 5-*cyclo*Hexane*spiro*di*cyclo*pentan-3-one-1:2-dicarboxylic anhydride (INGOLD and THORPE), 363.

$C_{12}H_{14}O_5$ Anhydride of 3-*cyclo*hexane*spiro*-1-methyl*cyclo*propane-1:1':2-tricarboxylic acid (INGOLD and THORPE), 379.

5-*cyclo*Hexane*spiro*di*cyclo*pentan-3-one-1:2-dicarboxylic acid (INGOLD and THORPE), 362.

cis-3-Hydroxy-4-*cyclo*hexyl*cyclo*butan-2-one-3:4-dicarboxylic anhydride (INGOLD and THORPE), 366.

$C_{12}H_{14}O_7$ Ethyl dihydrogen 5:5-dimethyldi*cyclo*pentan-3-one-1:2:4-tricarboxylate (INGOLD and THORPE), 383.

$C_{12}H_{16}O_6$ 3-*cyclo*Hexane*spiro*-1-methyl*cyclo*propane-1:1':2-tricarboxylic acid (INGOLD and THORPE), 379.

cis- and *trans*-3-Hydroxy-4-*cyclo*hexyl*cyclo*butan-2-one-3:4-dicarboxylic acids, and their salts (INGOLD and THORPE), 364.

$C_{12}H_{18}O_3$ 2:4-Dimethyl*cyclo*hexane 1:1-diacetic anhydride (KON and THORPE), 696.

$C_{12}H_{20}O_4$ 2:4-Dimethyl*cyclo*hexane-1:1-diacetic acid (KON and THORPE), 695.

$C_{12}H_{22}O_{11}$ Maltose, constitution of (IRVINE and DICK), 593; (HAWORTH and LEITCH), 809.

12 III

$C_{12}H_7O_2N$ ψ-1:8-*iso*Naphthoxazones, and their salts (DEY and GOSWAMI), 531.

$C_{12}H_9O_2N$ Indenyl-2- and -3-cyanoacetic acids (INGOLD and THORPE), 151.

$C_{12}H_9O_5N_3$ 5-Nitrophenol-2-azoresorcinol (MORGAN and EVENS), 1137.

$C_{12}H_{10}O_3N_2$ *N*-Nitroso-5:6:7:8-tetrahydro-ψ-1:8-*iso*naphthoxazone (DEY and GOSWAMI), 539.

$C_{12}H_{11}O_2N$ 5:6:7:8-Tetrahydro-ψ-1:8-*iso*naphthoxazone (DEY and GOSWAMI), 538.

$C_{12}H_{11}O_2Cl$ Allyl α-chlorocinnamates (WALKER and JAMES), 1247.

$C_{12}H_{11}O_4As$ *pp'*-Dihydroxydiphenylarsinic acid (FARGHER), 986.

$C_{12}H_{12}O_2N_2$ Ethyl 2-phenylglyoxaline-4-carboxylate (FARGHER and PYMAN), 1019.

$C_{12}H_{12}N_2Se_2$ Di-*m*-aminophenyl diselenide, and its hydrochloride (PYMAN), 171.

$C_{12}H_{12}ON_2$ 2-Ethylglyoxaline-4-carboxyanilide (FARGHER and PYMAN), 1017.

$C_{12}H_{12}O_3N_2$ ω-Imide of *aa'*dicyano-2-methyl*cyclo*pentane-1:1-diacetic acid (KON and THORPE), 697.

$C_{12}H_{18}O_2N_2$ ω-Imide of *aa'*-dicyano-β-methyl-β-ψ-butylglutaric acid (KON and THORPE), 702.

$C_{12}H_{17}ON_3$ Benzyl *iso*propyl ketone semicarbazone (KON and THORPE), 703.

$C_{12}H_{17}O_3N_3$ Semicarbazone of 5-*cyclo*hexane*spiro*di*cyclo*pentan-3-one-1-carboxylic acid (INGOLD and THORPE), 364.

$C_{12}H_{19}O_3N_3$ Semicarbazone of 5-*cyclo*hexane*spirocyclo*pentan-3-one-1-carboxylic acid (INGOLD and THORPE), 373.

12 IV

$C_{12}H_8O_4N_2Se_2$ Di-*m*-nitrophenyl diselenide (PYMAN), 170.

$C_{12}H_9O_8N_2As$ 3:3′-Dinitro-4:4′-dihydroxydiphenylarsinic acid (FARGHER), 986.

$C_{12}H_{11}O_6N_4As$ 3:3′-Dinitro-4:4′-diaminodiphenylarsinic acid (FARGHER), 989.

12 V

$C_{12}H_{13}O_2N_2ClAs$ 3:3′-Diamino-4:4′-dihydroxydiphenylarsenious chloride, dihydrochloride of (FARGHER), 987.

C_{13} Group.

$C_{13}H_{13}N$ α-Indenyl-3-*n*-butyronitrile (INGOLD and THORPE), 154.

$C_{13}H_{14}O_2$ *o*- and *p*-Hydroxybenzylidenemesityl oxide (GHOSH), 298.

$C_{13}H_{16}O_5$ *cis*-3-Hydroxy-4-*cyclo*hexyl-1-methyl*cyclo*butan-2-one-3:4-dicarboxylic anhydride (INGOLD and THORPE), 372.

cis-Lactonic anhydride from γ-hydroxy-β-*cyclo*hexyl-α-methyltricarballylic acid (INGOLD and THORPE), 371.

$C_{13}H_{18}O_3$ 5-*cyclo*Hexane*spiro*-2-ethyl*cyclo*pentan-3-one-1-carboxylic acid (INGOLD and THORPE), 379.

$C_{13}H_{18}O_6$ *cis*- and *trans*-3-Hydroxy-4-*cyclo*hexyl-1-methyl*cyclo*butan-2-one 3:4-dicarboxylic acids (INGOLD and THORPE), 371.

cis- and *trans*-Lactonic acids from γ-hydroxy-β-*cyclo*hexyl-α-methyltricarballylic acid, and their silver salts (INGOLD and THORPE), 368.

$C_{13}H_{18}N_2$ 2:5-Dimethyl-1-*n*-butylbenziminazole, and its picrate (REILLY and HICKINBOTTOM), 178.

$C_{13}H_{20}O_4$ Acetyl derivative of 5-*cyclo*hexane*spirocyclo*pentan-3-ol-1-carboxylic acid (INGOLD and THORPE), 374.

$C_{13}H_{20}O_7$ *cis*- and *trans*-γ-Hydroxy-β-*cyclo*hexyl-α-methyltricarballylic acids, barium salts (INGOLD and THORPE), 369.

13 III

$C_{13}H_7O_4N$ 6-Nitro-1:2-α-naphthapyrone (DEY and GOSWAMI), 540.

$C_{13}H_8O_2N_2$ Quinolinanil (GHOSH), 1103.

$C_{13}H_9O_2N$ 9-Methyl ψ-1:8-*iso*naphthoxazone, and its salts (DEY and GOSWAMI), 539.

$C_{13}H_9O_2N_3$ Quinolinylphenylhydrazine (GHOSH), 1103.

$C_{13}H_{12}ON_2$ Harmine, and its salts (PERKIN and ROBINSON), 946.

Methylnorharmine (PERKIN and ROBINSON), 951.

$C_{13}H_{12}O_3N_2$ Nitroso-5:6:7:8-tetrahydro-9-methyl-ψ-1:8-*iso*naphthoxazone (DEY and GOSWAMI), 539.

$C_{13}H_{13}ON$ Aceto-β-naphthylmethylamide (MORGAN and EVANS), 1143.

$C_{13}H_{13}O_2N$ 5:6:7:8-Tetrahydro-9-methyl-ψ-1:8-*iso*naphthoxazone (DEY and GOSWAMI), 539.

$C_{13}H_{14}ON_2$ Harmaline, and its salts (PERKIN and ROBINSON), 951.

$C_{13}H_{14}O_2N_2$ Keto*iso*normethyltetrahydroharmine (PERKIN and ROBINSON), 959.

$C_{13}H_{14}O_2N_4$ 2-Acetylamino-4-*p*-acetylaminophenylglyoxaline, and its hydrochloride (FARGHER and PYMAN), 240.

$C_{13}H_{15}O_2N_3$ ω-Imide of αα′-dicyano-2-methyl*cyclo*hexane-1:1-diacetic acid (KON and THORPE), 694.

$C_{13}H_{19}O_4N_3$ ω-Imide of αα′-dicarbamyl-2-methyl*cyclo*hexane-1:1-diacetic acid (KON and THORPE), 694.

$C_{13}H_{20}ON_2$ 4-Acetyltolylene-4-*N*-*n*-butyldiamines (REILLY and HICKINBOTTOM), 176.

$C_{13}H_{21}O_4N$ Meteloidine, and its salts (KING), 501.

$C_{13}H_{23}ON_3$ Tributylcarbamide (WERNER), 1013.

13 IV

$C_{13}H_{10}O_2NI$ ψ-1:8-*iso*Naphthoxazone-*N*-methiodide (DEY and GOSWAMI), 538.

C_{14} Group.

$C_{14}H_8O_2$ Phenanthraquinone, basic properties of (KNOX and WILL), 850.

$C_{14}H_{12}O$ Deoxybenzoin, condensation of aldehydes with (DAS and GHOSH), 817; (SINGH and MAZUMDER), 821.

$C_{14}H_{13}N$ α-Indenyl-3-allylacetonitrile (INGOLD and THORPE), 155.

$C_{14}H_{14}O_2$ Piperonylidenemesityl oxide (GHOSH), 298.

$C_{14}H_{15}N$ α-Indenyl-3-*n*-valeronitrile (INGOLD and THORPE), 154.

$C_{14}H_{16}N_2$ Diphenylethylenediamine, preparation of, and its sulphate (BENNETT), 576.

$C_{14}H_{18}O_5$ Anhydride of *cis*-lactonic acid, $C_{14}H_{20}O_6$ (INGOLD and THORPE), 382.

Ethyl hydrogen 5-*cyclo*hexane*spiro*di*cyclo*pentan-3-one-1:4-dicarboxylate (INGOLD and THORPE), 361.

$C_{14}H_{20}O_6$ *cis*- and *trans*-Lactonic acids from γ-hydroxy-β-*cyclo*hexyl-α-ethyltricarballylic acid, and their silver salts (INGOLD and THORPE), 380.

$C_{14}H_{22}O_7$ *cis*- and *trans*-γ-Hydroxy-β-*cyclo*hexyl-α-ethyltricarballylic acids, and their barium salts (INGOLD and THORPE), 381.

14 III

$C_{14}H_8O_{16}N_{10}$ 2:4:6:2′:4′:6′-Hexanitrodiphenylethylenedinitroamine (BENNETT), 577.

$C_{14}H_{10}ON_2$ Phenylphthalalazone, preparation of (MITTER and SEN), 1147.

$C_{14}H_{10}O_2N_2$ Phenylazophthalide (MITTER and SEN), 1147.

$C_{14}H_{10}O_{12}N_6$ Hexanitrodiphenylethylenediamine (BENNETT), 578.

$C_{14}H_{10}N_4As_2$ 5:5′-Arseno-1:3:1′:3′-benzodiazole, and its dihydrochloride (BAXTER and FARGHER), 1376.

$C_{14}H_{11}O_2N$ 4:9-Dimethyl-ψ-1:8-*iso*naphthoxazone, and its salts (DEY and GOSWAMI), 539.

$C_{14}H_{12}O_2N_2$ Phthalaldehydic acid phenylhydrazone (MITTER and SEN), 1146.

$C_{14}H_{13}O_2N$ Ethyl indenyl-2- and -3-cyanoacetates (INGOLD and THORPE), 150.

$C_{14}H_{14}ON_2$ Methylharmine, and its salts (PERKIN and ROBINSON), 947.

$C_{14}H_{14}O_3N_2$ Nitroso-5:6:7:8-tetrahydro-4:9-dimethyl-ψ-1:8-*iso*naphthoxazone (DEY and GOSWAMI), 540.

$C_{14}H_{15}O_2N$ 5:6:7:8-Tetrahydro-4:9-dimethyl-ψ-1-8-*iso*naphthoxazone (DEY and GOSWAMI), 540.

$C_{14}H_{16}O_2N_4$ 2-Acetylamino-5-*p*-acetylaminophenyl-4-methylglyoxaline, and its hydrochloride (FARGHER and PYMAN), 251.

$C_{14}H_{17}O_3N_3$ ω-Imide of αα′-dicyano-2:4-dimethyl*cyclo*hexane-1:1-diacetic acid (KON and THORPE), 695.

$C_{14}H_{19}ON_2$ Methyltetrahydroharmine, and its salts (PERKIN and ROBINSON) 953.

14 IV

$C_{14}H_8O_4N_2As_2$ 1:2:1′:2′-Tetrahydro-4-arsenobenzodioxazolone (FARGHER), 991.

$C_{14}H_{12}O_2NI$ ψ-1:8-*iso*Naphthoxazone-*N*-ethiodide (DEY and GOSWAMI), 538.

$C_{14}H_{14}O_4N_2S$ Harmine methohydroxide sulphonic anhydride (PERKIN and ROBINSON), 950.

$C_{14}H_{16}O_2N_2As_2$ 4:4′-Dihydroxy-5:5′-diamino-3:3′-dimethylarsenobenzene, hydrochloride of $(+ 2H_2O)$, (FARGHER), 990.

$C_{14}H_{16}O_4N_2S$ Harmaline methohydroxide sulphonic anhydride (PERKIN and ROBINSON), 953.

C_{15} Group.

$C_{15}H_{16}O$ Cinnamylidenemesityl oxide (GHOSH), 299.

$C_{15}H_{16}O_6$ Anhydro-ester from ethyl dihydrogen *cyclo*hexane*spiro*di*cyclo*pentan-3-one-1:2:4-tricarboxylate (INGOLD and THORPE), 361.

$C_{15}H_{18}O_7$ Ethyl dihydrogen *cyclo*hexane*spiro*di*cyclo*pentan-3-one-1:2:4-tricarboxylate (INGOLD and THORPE), 360.

15 III

$C_{15}H_{10}O_3N_2$ Phenylphthalazonecarboxylic acid (MITTER and SEN), 1148.

$C_{15}H_{11}N_4Br$ 2-Phenyl-4-*p*-bromobenzeneazoglyoxaline (FARGHER and PYMAN), 256.

$C_{15}H_{12}O_4N_2$ Phthalonic acid phenylhydrazone (MITTER and SEN), 1147.

$C_{15}H_{13}O_2N_3$ ω-Imide of αα′-dicyano-β-benzyl-β-methylglutaric acid (KON and THORPE), 704.

$C_{15}H_{13}N_4Br$ Base, from reduction of 2-phenyl-4-*p*-bromobenzeneazoglyoxaline (FARGHER and PYMAN), 257.

$C_{15}H_{15}O_2N$ Ethyl α-indenyl-2- and -3-α-cyanopropionates (INGOLD and THORPE), 152.

$C_{15}H_{19}O_3N$ *cyclo*Pentane-1:1-diacetic semianilide (KON and THORPE), 701.

$C_{15}H_{20}ON_2$ Dehydro*iso*methyltetrahydroharmine methohydroxide, and its salts (PERKIN and ROBINSON), 957.

$C_{15}H_{22}O_2N_2$ 3:4-Diacetyltolylene-4-*N*-*n*-butylamine (REILLY and HICKINBOTTOM), 177.

$C_{15}H_{23}O_6N$ Ethyl α-cyano-γ-methylbutane-αβδ-tricarboxylate (THORPE), 683.

15 IV

$C_{15}H_{13}O_2NBr$ ψ-1:8-*iso*Naphthoxazone *N*-allyl bromide (DEY and GOSWAMI), 538.

C_{16} Group.

$C_{16}H_{14}N_6$ 2:5-Bisbenzeneazo-4-methylglyoxaline (FARGHER and PYMAN), 250.

$C_{16}H_{18}N_2$ Camphanoquinoxaline, and its optical activity (SINGH and MAZUMDER), 574.

16 III

$C_{16}H_9O_2N$ ψ-Benzo-1:8-*iso*naphthoxazone (DEY and GOSWAMI), 540.

$C_{16}H_9O_7N_5$ Azotrinitro-β-naphthol (MORGAN and EVENS), 1135.

$C_{16}H_{10}O_5N_4$ *p*-Nitrobenzene-1-azo-4-nitro-β-naphthol (MORGAN and EVENS), 1134

$C_{16}H_{10}O_6N_4$ Azodinitro-β-naphthol (MORGAN and EVENS), 1135.

$C_{16}H_{10}N_2Cl_3$ *s*-Trichlorobenzeneazo-β-naphthylamine (NORMAN), 678.
$C_{16}H_{11}O_3N_3$ Benzene-1-azo-4-nitro-β-naphthol (MORGAN and EVENS), 1134.
$C_{16}H_{11}O_5N_3$ 4-Nitro-β-naphthol-1-azoresorcinol (MORGAN and EVENS), 1131.
$C_{16}H_{12}N_3Cl$ *o*-Chlorobenzeneazo-β-naphthylamine (NORMAN), 675.
β-Naphthalenediazoamino-*o*-chlorobenzene (NORMAN), 676.
$C_{16}H_{13}ON_3$ 2-Phenylglyoxaline-4-carboxyanilide (FARGHER and PYMAN), 1018.
$C_{16}H_{14}O_2N_2$ Phenylhydrazone of aldehyde, from hemlock tannin (MANNING and NIERENSTEIN), 668.
$C_{16}H_{14}N_4As_2$ Dimethyl-5:5′-arseno-1:3:1′:3′-benzodiazoles, and their dihydrochlorides (BAXTER and FARGHER), 1377.
$C_{16}H_{15}O_2N_3$ ω-Imide of αα′-dicyano-β-benzyl-β-ethylglutaric acid (KON and THORPE), 704.
$C_{16}H_{17}O_2N$ Ethyl α-indenyl-3-α-cyano-*n*-butyrate (INGOLD and THORPE), 153.
$C_{16}H_{19}O_2N_3$ ω-Imide-αα′-dicyano-2-methyl-5-*iso*propylidene*cyclo*hexane-1:1-diacetic acid (KON and THORPE), 696.
$C_{16}H_{19}O_4N$ Ethyl ω-cyano-*m*-methylbenzylmalonate (GOUGH and THORPE), 1163.
$C_{16}H_{24}O_2N_2$ *iso*Methyltetrahydroharmine methohydroxide methyl ether (PERKIN and ROBINSON), 955.

16 IV

$C_{16}H_{13}O_8N_2As$ *pp′*-Dioxalylaminodiphenylarsinic acid (FARGHER), 988.
$C_{16}H_{16}O_2NI$ ψ-1:8-*iso*Naphthoxazone *N*-*n*-butyl iodide (DEY and GOSWAMI), 538.
$C_{16}H_{16}O_2N_2Se_2$ Di-*m*-acetylaminophenyl diselenide (PYMAN), 172.
$C_{16}H_{18}ONCl$ Chlorophenyliminocamphors, and their optical activity (SINGH and MAZUMDER), 572.
$C_{16}H_{18}ONBr$ Bromophenyliminocamphors, and their optical activity (SINGH and MAZUMDER), 570.
$C_{16}H_{30}ONCl$ *o*- and *m*-Chlorophenyl aminocamphor (FORSTER and SPINNER), 892.

C_{17} Group.

$C_{17}H_{15}N_3$ Benzeneazo-β-naphthylmethylamine (MORGAN and EVANS), 1142.
$C_{17}H_{16}N_4$ 2-Amino-5-*p*-benzylideneaminophenyl-4-methylglyoxaline, and its acetate (FARGHER and PYMAN), 252.
$C_{17}H_{22}O_7$ Diethyl hydrogen *cyclo*hexane*spiro*di*cyclo*pentan-3-one-1:2:4-tricarboxylate, and its potassium salt (INGOLD and THORPE), 360.

17 III

$C_{17}H_{11}O_2N$ 4-Methyl-ψ-benzo-1:8-*iso*naphthoxazone (DEY and GOSWAMI), 540.
$C_{17}H_{12}O_6N_4$ 2:4-Dinitrophenylnitro-β-naphthylmethylamine (MORGAN and EVANS), 1145.
$C_{17}H_{13}O_4N_3$ 2:4-Dinitrophenyl-β-naphthylmethylamine (MORGAN and EVANS), 1144.
$C_{17}H_{14}O_2N_4$ *p*-Nitrobenzene-1-azo-β-naphthylmethylamine (MORGAN and EVANS), 1143.
Nitrotolueneazo-β-naphthylamines (NORMAN), 678.
$C_{17}H_{14}N_3Br$ Bromo-*o*- and -*p*-tolueneazo-β-naphthylamines (NORMAN), 676.
β-Naphthalenediazoaminobromotoluenes (NORMAN), 676.
$C_{17}H_{17}O_2N$ Ethyl α-indenyl-3-α-cyanoallylacetate (INGOLD and THORPE), 155.

$C_{17}H_{17}O_2N_3$ ω-Imide of αα′dicyano-β-methyl-β-(α-benzylethyl) glutaric acid (KON and THORPE), 703.

$C_{17}H_{17}O_5N$ Glycol *o*-xylyl ether *p*-nitrobenzoate (BOYD and THOMAS), 1243.

$C_{17}H_{19}O_2N$ Ethyl α-indenyl-3-α-cyano-*n*- and -*iso*-valerates (INGOLD and THORPE), 154.

$C_{17}H_{19}O_3N$ *m*- and *p*-Carboxyphenyliminocamphor (FORSTER and SPINNER), 892.

$C_{17}H_{21}ON$ Tolyliminocamphors, and their optical activity (SINGH and MAZUMDER), 568.

$C_{17}H_{21}O_2N$ *o*-Methoxyphenyliminocamphor, and its optical activity (SINGH and MAZUMDER), 575.

$C_{17}H_{21}O_3N$ *m*- and *p*-Carboxyphenylaminocamphor (FORSTER and SPINNER), 893.

$C_{17}H_{21}O_4N$ Hyoscine, stereochemistry of, and its salts (KING), 476, 974.

$C_{17}H_{26}O_2N_2$ *iso*Methyltetrahydroharmine methohydroxide ethyl ether (PERKIN and ROBINSON), 956.

17 IV

$C_{17}H_{13}O_6N_3S$ Toluene-*p*-sulphon-2:4-*di*nitro-α-naphthylamide (MORGAN and EVENS), 1130.

$C_{17}H_{18}O_2NI$ ψ-1:8-*iso*Naphthoxazone *N*-amyl iodide (DEY and GOSWAMI), 538.

C_{18} Group.

$C_{18}H_{17}N$ Benzyl-β-naphthylmethylamine (MORGAN and EVANS), 1144.

$C_{18}H_{17}N_3$ 2-β-Naphthalenediazoamino-*p*-xylene (NORMAN), 677.

m- and *p*-Xyleneazo-β-naphthylamines (NORMAN), 674.

$C_{18}H_{34}O_6$ *n*-Heptyl tartrate, and its rotation dispersion (FRANKLAND and GARNER), 655.

18 III

$C_{18}H_{15}ON$ Benzo-β-naphthylmethylamide (MORGAN and EVANS), 1144.

$C_{18}H_{18}N_4As_2$ 2:7:2′:7′-Tetramethyl-5:5′-arseno-1:3:1′:3′-benzodiazole, and its dihydrochloride (BAXTER and FARGHER), 1379.

$C_{18}H_{19}O_4N$ Anil from *cis*-3-hydroxy-4-*cyclo*hexyl*cyclo*butan-2-one-3:4-dicarboxylic acid (INGOLD and THORPE), 367.

$C_{18}H_{21}O_2N$ Ethyl α-indenyl-3-α-cyano*iso*hexoate (INGOLD and THORPE), 156.

$C_{18}H_{21}O_5N$ Anilic acid from *cis*-3-hydroxy-4-*cyclo*hexyl*cyclo*butan-2-one-3:4-dicarboxylic acid (INGOLD and THORPE), 366.

$C_{18}H_{22}O_3N_2$ *p*-Acetylaminophenyliminocamphor (FORSTER and SPINNER), 893.

$C_{18}H_{23}O_3N$ 2:4-Dimethyl*cyclo*hexane-1:1-diacetic semianilide (KON and THORPE), 696.

$C_{18}H_{27}O_3N$ Capsaicin (LAPWORTH and ROYLE) 1109.

18 IV

$C_{18}H_{12}ON_3Cl_3$ Acetyl derivative of *s*-trichlorobenzeneazo-β-naphthylamine (NORMAN), 678.

$C_{18}H_{14}ON_3Cl$ Acetyl derivative of *o*-chlorobenzeneazo-β-naphthylamine (NORMAN), 675.

C_{19} Group.

$C_{19}H_{20}O_6$ Dihydrocryptopidenic acid (PERKIN), 764.

$C_{19}H_{26}O_7$ Ethyl *cyclo*hexane*spiro*di*cyclo*pentan-3-one-1:2:4-tricarboxylate, and its sodium salt (INGOLD and THORPE), 358.

19 III

$C_{19}H_{11}O_5N$ Resorcinolquinolinein, and its silver salt (GHOSH), 1103.
$C_{19}H_{11}O_7N$ Phloroglucinolquinolinein (GHOSH), 1104.
$C_{19}H_{14}O_2N_4$ *m*-Phenylenediaminequinolinein (GHOSH), 1104.
$C_{19}H_{14}O_4N_4$ 2:4-Diaminophenolquinolinein (GHOSH), 1105.
$C_{19}H_{15}O_3N$ Benzoyl derivative of 5:6:7:8-tetrahydro-ψ-1:8-*iso*naphthoxazone (DEY and GOSWAMI), 539.
$C_{19}H_{16}O_2N_4$ Acetyl derivatives of nitrotolueneazo-β-naphthylamines (NORMAN), 678.
$C_{19}H_{19}O_2N_3$ *p*-Nitrobenzeneazotetrahydroharmine (PERKIN and ROBINSON), 963.
$C_{19}H_{23}O_2N$ Ethyl α-indenyl-3-α-cyano*iso*heptoate (INGOLD and THORPE), 156.
$C_{19}H_{23}O_4N$ Porphyroxine, and its salts (RAKSHIT), 455.
$C_{19}H_{29}O_3N$ Methylcapsaicin (LAPWORTH and ROYLE), 1113.

19 IV

$C_{19}H_{14}O_2NCl$ ψ-1:8-*iso*Naphthoxazone *N*-benzyl chloride (DEY and GOSWAMI), 538.
$C_{19}H_{16}ON_2Br$ Acetyl derivatives of bromotolueneazo-β-naphthylamines (NORMAN), 676.
$C_{19}H_{20}O_4N_4S$ Benzeneazotetrahydroharminesulphonic acid (PERKIN and ROBINSON), 964.

C_{20} Group.

$C_{20}H_{18}O_6$ Dioxy-ψ-cryptopidene (PERKIN), 773.
$C_{20}H_{18}O_7$ Trioxy-ψ-cryptopidene (PERKIN), 773.
$C_{20}H_{20}O_4$ *iso*-ψ-Berberidene (PERKIN), 778.
Cryptopidenes (PERKIN), 744, 772, 776, 786.
$C_{20}H_{20}O_5$ Hydroxycryptopidene (PERKIN), 742.
Ketodihydrocryptopidenes (PERKIN), 763, 777.
$C_{20}H_{20}O_8$ Ketohydroxydihydro*iso*cryptopidenic acid (PERKIN), 790.
$C_{20}H_{22}O_4$ Dihydrocryptopidene (PERKIN), 762.
$C_{20}H_{22}O_5$ Dihydro-α-*iso*cryptopidol (PERKIN), 758.
$C_{20}H_{24}O_4$ Tetrahydrocryptopidene (PERKIN), 744.
$C_{20}H_{28}O_7$ Ethyl *cyclo*hexane*spiro*-2-methyldi*cyclo*pentan-3-one-1:2:4-tricarboxylate (INGOLD and THORPE), 368.
$C_{20}H_{38}O_{11}$ Heptamethylmethylmaltoside (HAWORTH and LEITCH), 814.

20 III

$C_{20}H_{19}ON_3$ Acetyl derivatives of xyleneazo-β-naphthylamines (NORMAN), 674.
$C_{20}H_{21}ON$ α- and β-Naphthyliminocamphors, and their optical activity (SINGH and MAZUMDER), 573.
$C_{20}H_{23}ON$ α- and β-Naphthylaminocamphor (FORSTER and SPINNER), 891.

20 IV

$C_{20}H_{14}O_3NBr$ ψ-1:8-*iso*Naphthoxazone *N*-phenylacetyl bromide (DEY and GOSWAMI), 538.
$C_{20}H_{22}O_4N_4S$ Benzeneazomethyltetrahydroharminesulphonic acid (PERKIN and ROBINSON), 965.

C_{21} Group.

$C_{21}H_{16}O_2$ *p*-Hydroxybenzylidenedeoxybenzoin (SINGH and MAZUMDER) 824.
Salicylidenedeoxybenzoin (SINGH and MAZUMDER), 822.

$C_{21}H_{16}N_8$ 2:4:5-Trisbenzeneazoglyoxaline (FARGHER and PYMAN), 237.
$C_{21}H_{20}O_6$ Curcumin (GHOSH), 292.
$C_{21}H_{32}O_8$ Ethyl *cyclo*hexane*spiro*-1-methyl*cyclo*propane-1:1′:1′:2-tetracarboxylate (INGOLD and THORPE), 357.

21 III

$C_{21}H_{15}ON$ 4-Hydroxy-2:3-diphenylquinoline (SINGH and MAZUMDER), 823.
$C_{21}H_{13}OCl$ 2:3-Diphenylbenzopyronium chloride (DAS and GHOSH), 819; (SINGH and MAZUMDER), 822.
$C_{21}H_{19}O_4Br$ Bromocurcumin (GHOSH), 295.
$C_{21}H_{21}O_3N_3$ *m*-Dimethylaminophenolquinolinein (GHOSH), 1105.
$C_{21}H_{21}O_4N$ Anhydrocryptopines, and their salts (PERKIN), 736, 780.
$C_{21}H_{21}O_7N_3$ Disemicarbazone of trioxy-ψ-cryptopidene (PERKIN), 773.
$C_{21}H_{23}O_4N$ ψ-Anhydrodihydrocryptopine, and its salts (PERKIN), 769.
Dihydroanhydro*iso*cryptopines and their salts (PERKIN), 748, 781.
$C_{21}H_{23}O_5N$ Cryptopine (PERKIN), 713.
$C_{21}H_{23}O_5N_3$ Semicarbazones of ketodihydrocryptopidenes (PERKIN), 764, 777.
$C_{21}H_{25}O_4N$ Dihydroanhydro-ψ-cryptopine, and its picrate (PERKIN), 775.
Dihydroanhydrodihydrocryptopine, and its salts (PERKIN), 754.
Dihydroanhydro-ψ-methylberberine, and its salts (PERKIN), 779.
Tetrahydroanhydro*iso*cryptopine, and its salts (PERKIN), 751.

21 IV

$C_{21}H_{15}O_3N_2As$ 4-Methylphenanthraphenazine-2-arsinic acid (BAXTER and FARGHER), 1378.
$C_{21}H_{19}O_3N_4Br$ Triacetyl derivative of base, $C_{15}H_{13}N_4Br$ (FARGHER and PYMAN), 258.
$C_{21}H_{22}O_4NCl$ ψ-Cryptopine chloride (PERKIN), 766.
$C_{21}H_{22}O_4NBr$ ψ-Cryptopine bromide (PERKIN), 767.
$C_{21}H_{22}O_4NI$ ψ-Cryptopine iodide (PERKIN), 768.
$C_{21}H_{23}O_8NS$ ψ-Cryptopine hydrogen sulphate (PERKIN), 768.

C_{22} Group.

$C_{22}H_{18}O_3$ Vanillylidenedeoxybenzoin (SINGH and MAZUMDER), 824.
$C_{22}H_{22}O_5$ Divanillylidenemesityl oxide (GHOSH), 299.

22 III

$C_{22}H_{23}O_3N$ *p*-Benzeneazophenyliminocamphor, and its optical activity, (SINGH and MAZUMDER), 574.
$C_{22}H_{23}ON_3$ *p*-Benzeneazophenylaminocamphor (FORSTER and SPINNER), 894.
$C_{22}H_{25}O_4N$ Dihydroanhydromethylcryptopine, and its salts (PERKIN), 740.
n- and ψ-Dihydromethyl*iso*anhydrocryptopines, and their salts (PERKIN), 782.
$C_{22}H_{25}O_6N$ Dioxymethyl*iso*anhydrodihydrocryptopine (PERKIN), 739.
$C_{22}H_{27}O_4N$ Anhydrotetrahydromethylcryptopine (PERKIN), 752.
Dihydro*iso*anhydrodihydromethylcryptopine (PERKIN), 757.
Tetrahydromethyl*iso*anhydrocryptopine (PERKIN), 788.
Tetrahydroanhydromethylcryptopine, and its platinichloride (PERKIN), 744.
$C_{22}H_{27}O_5N$ Dihydromethylcryptopine (PERKIN), 746.

$C_{22}H_{29}O_4N$ Dihydroanhydrotetrahydromethylcryptopine, and its salts (PERKIN), 760.

C_{23} Group.

$C_{23}H_{18}O$ Cinnamylidenedeoxybenzoin, and its hydrochloride (SINGH and MAZUMDER), 825.

$C_{23}H_{28}O_{15}$ Dryophantin (NIERENSTEIN), 1330.

23 III

$C_{23}H_{16}N_4S_6$ Substance, from benzylidene chloride and the potassium salt of 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole (RÂY, GUHA, and DAS), 1311.

$C_{23}H_{19}O_2N$ Ethyl 2:3′-di-indenyl-3-cyanoacetate (INGOLD and THORPE), 151.

$C_{23}H_{21}ON$ *p*-Dimethylaminobenzylidenedeoxybenzoin (SINGH and MAZUMDER), 825.

$C_{23}H_{22}O_6Br_6$ Dibromodimethylcurcumin tetrabromide (GHOSH), 296.

$C_{23}H_{23}O_6Br$ Bromodimethylcurcumin (GHOSH), 296.

23 IV

$C_{23}H_{16}ON_3Cl$ Benzoyl derivative of *o*-chlorobenzeneazo-β-naphthylamine (NORMAN), 675.

C_{24} Group.

$C_{24}H_{40}N_2$ Conessine, and its hydrogen oxalate (PYMAN), 164.

24 III

$C_{24}H_{15}O_3N_4$ Benzoyl derivatives of nitrotolueneazo-β-naphthylamine (NORMAN), 678.

$C_{24}H_{35}ON_3$ Holarrhenine, and its hydrobromide (PYMAN), 165.

24 IV

$C_{24}H_{15}ON_3Br$ Benzoyl derivatives of bromotolueneazo-β-naphthylamine (NORMAN), 676.

$C_{24}H_{24}O_4N_4As_2$ 3:3′:3″:3‴-Tetra-amino-4:4′:4″:4‴-tetrahydroxytetraphenyldiarsine, tetrahydrochloride of (FARGHER), 987.

C_{25} Group.

$C_{25}H_{16}N_6S_9$ Substance, from bromoform or iodoform and the potassium salt of 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole (RÂY, GUHA, and DAS), 1309.

$C_{25}H_{17}OCl$ 2:3-Diphenylnaphthapyronium chloride (SINGH and MAZUMDER), 823.

$C_{25}H_{21}ON_3$ Benzoyl derivatives of xyleneazo-β-naphthylamines (NORMAN), 674.

$C_{25}H_{22}O_8Br_6$ Dibromodiacetylcurcumin tetrabromide (GHOSH), 296.

$C_{25}H_{23}O_8Br$ Bromodiacetylcurcumin (GHOSH), 296.

$C_{25}H_{25}O_5N$ Dihydrocryptopidenic anilide (PERKIN), 764.

25 IV

$C_{25}H_{15}O_2N_7S_9$ Substance, from chloropicrin and the potassium salt of 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole (RÂY, GUHA, and DAS), 1311.

C_{26} Group.

$C_{26}H_{32}O_2N_2$ *m*-Phenylenebisiminocamphor, and its optical activity (SINGH and MAZUMDER), 575.

$C_{26}H_{40}O_2N_2$ Acetylholarrhenine (PYMAN), 165.

C_{27} Group.

$C_{27}H_{32}O_{10}$ Dicarbethoxy*iso*curcumin (GHOSH), 297.

27 III

$C_{27}H_{26}O_{10}Br_6$ Dibromodicarbethoxycurcumin tetrabromide (GHOSH), 296.

$C_{27}H_{27}O_{10}Br$ Bromodicarbethoxycurcumin (GHOSH), 295.

$C_{27}H_{27}O_{10}Br_5$ Bromodicarbethoxycurcumin tetrabromide (GHOSH), 295.

C_{28} Group.

$C_{28}H_{24}O_6$ Benzylidenecurcumin (GHOSH), 294.

C_{29} Group.

$C_{29}H_{29}O_6N_3$ Substance, from curcumin and nitrosodimethylaniline (GHOSH), 294.

C_{30} Group.

$C_{30}H_{12}O_3N_6S_9$ Substance, from tribromoresorcinol and the potassium salt of 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole (RÂY, GUHA, and DAS), 1311.

C_{32} Group.

$C_{32}H_{36}O_2N_2$ *pp*-Diphenylenebisiminocamphor (FORSTER and SPINNER), 893.

C_{36} Group.

$C_{36}H_{28}O_4$ 3:4-Methylenedioxybenzamarone (DAS and GHOSH), 820.

$C_{36}H_{30}O_2$ *p*-Methylbenzamarone ($+\frac{1}{2}H_2O$), (DAS and GHOSH), 820.

ERRATA.

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Page	Line	
814	7*	*for* "α_D^-" *read* "$[\alpha]_D$."
816	9	*for* "α_D" *read* "$[\alpha]_D$."
816	1	*for* "0·1060 H_2O" *read* "0·1006 H_2O."

Contents, p. i, line 14, p. 821, in title and headlines pp. 821–825 *for* "MAZUMDAR" *read* "MAZUMDER."

Contents, p. i, line 5, p. 1140, in title and headlines pp. 1140–1144 *for* "FREDERICK PAGE EVENS" *read* "FREDERICK PAGE EVANS."

* From bottom.